16ENV02 Black Carbon

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1 Overview

The measurement of particles in the air characterised as black carbon is important both for their role in climate change and as a measure of combustion products associated with health effects. Measurements are made very widely, and compact, precise, real-time, relatively inexpensive instruments are available. Although it is conceptually a simple measure of the light-absorbing properties of airborne particles, the metric does not currently have SI traceability, with consequences for the comparability and interpretation of data. The project made substantial steps towards providing a workable solution to this major problem, using a combination of primary methods (which do not need to be calibrated with a black carbon calibration sample), black carbon reference sources, and a robust calibration protocol that addresses the fact that commonly-used instruments will have more than one type of measurement artefact.

2 Need

The quantity of airborne particles loosely described as black carbon has been widely measured by various optical methods since the early 20th century, because instruments for this are relatively simple and reliable. The dominant sources have changed over the decades, from domestic and industrial coal burning to vehicle combustion emissions, with more recent contributions from wood-burning.

Black carbon has been identified as the second most important climate forcing agent behind CO_2, contributing an amount of radiative forcing nearly 30 % that of current CO_2 concentrations. Airborne particles have serious human health effects across Europe and worldwide. In 2011, about 430,000 premature deaths in the EU were attributed to fine particulate matter (PM). Studies suggest that black carbon is a better indicator of harmful particulate substances from combustion sources than PM mass concentration.

Although black carbon measurement is in principle a simple optical measurement of absorption, characterised by the aerosol light absorption coefficient, traceability is hampered by the fact that routine monitors determine the absorption of particulate matter collected on a fibrous filter. While the optical absorption measurement itself can be done accurately, the presence of the filter has a large effect, due to internal scattering within the filter, which can increase absorption by a factor of five, and shadowing effects as the filter accumulates material. Empirical but non-traceable correction factors are then incorporated into the conversion from light absorption coefficient into the reported particle mass concentration; these correction factors need to be replaced with properly determined calibration factors in order to standardise the measurement results and ensure confidence and comparability in the field.

3 Objectives

The overriding objective of the project was, for the first time, to bring SI traceability to field of black carbon measurements, so that their accuracy and value would be greatly increased. The specific objectives were:

1. To establish a set of well-defined physical parameters, such as aerosol light absorption coefficients and mass absorption coefficients, which together can be used to quantify black carbon mass concentrations with traceability to primary standards.

2. To develop and characterise black carbon standard reference materials (SRMs), representative of atmospheric aerosols, together with methods for using them to calibrate field black carbon monitors.

3. To develop a traceable, primary method for determining aerosol absorption coefficients at specific wavelengths that are to be defined for the benefit of users. The method should have defined uncertainties and a quantified lowest detection limit.

4. To develop a validated transfer standard for the traceable calibration of established absorption photometers such as multi angle absorption photometers, aethalometers and particle absorption photometers. The transfer standard should make use of the black carbon SRMs (developed in objective 2) and associated portable instrumentation characterised by the primary method (from objective 3).

5. To facilitate the take-up of the technology and measurement infrastructure developed in the project by standards developing organisations (CEN, ISO) and end users (e.g. Environmental Protection Agency (EPA), European Environment Agency (EEA), World Meteorological Organisation-Global Atmosphere Watch (WMO-GAW), the ACTRIS (Aerosols, Clouds, and Trace gases Research InfraStructure Network) Project).

4 Results

4.1 Objective 1: Physical parameters for traceable quantification of black carbon mass concentrations

4.1.1 Introduction

The aim of this objective was to define the physical properties of aerosols (and the particles within them), in a way that clarifies how traceability to the SI can be established. The determination of black carbon by measuring the light attenuation of particle contaminants applied to a filter is a common technique for monitoring soot concentrations. Conceptually, there are two steps to these measurements. First, the determination of the optical absorption of the particles. This is not easy due to cross interferences between the scattering of light by particles and the filter substrate. And second, the conversion of particle absorption into particulate mass assuming a mass absorption coefficient (MAC). The composition and optical properties of soot-like particles change significantly when combustion sources change, for example, from coal combustion to vehicle exhaust gases or due to atmospheric aging processes such as the formation of light scattering coatings, which has a significant influence on the relationship between absorption and black carbon mass concentration. Methods for measuring aerosol light absorption together with factors that influences the uncertainties and might cause technical limitations were also provided.

4.1.2 Relevant particle and gas properties

Light scattering and absorption by gases

The absorption and scattering of light due to gases must be considered in two ways. On the one hand, instruments can be calibrated with gases with known Rayleigh scattering coefficient or absorption cross section, on the other hand absorbing gases can influence the measurements of the particle light scattering or absorption coefficients.

Rayleigh scattering

Scattering of light by gas molecules is described by the Rayleigh scattering theory. The total scattering coefficient of an aerosol is measured in a nephelometer and has to be corrected for the Rayleigh scattering of the air. A study of the Rayleigh scattering coefficient of the atmosphere also takes into account deviations from the known Rayleigh scattering phase function due to the anisotropy of the molecules. Deviations of up to 1.5 % can occur in some scattering angle ranges due to anisotropy. Furthermore, the wavelength dependence of the Rayleigh scattering coefficients was parameterised by the dispersion of the refractive index. Deviations from other studies of 1 % were found in wavelength ranges between 350 and 1000 nm. Measurements of particle light scattering and extinction have to be corrected for Rayleigh scattering. The uncertainty caused by correction of the Rayleigh scattering must be investigated.

Absorption by gases

Absorption of radiation by gas molecules can have an influence on the measurement of the particle absorption coefficient. In the wavelength range of 350 to 1000 nm, NO_2 and water are the most important absorbers and must be considered. Concentrations of absorbing gases such as NO_2, O_3, and SO_2 can vary over orders of magnitude.

In addition to the undesired cross-sensitivity to absorbing gases, gases with known absorption cross-sections are used for calibration of in-situ aerosol absorption instruments, e.g. photoacoustic absorption photometers and photothermal interferometery systems. Figure I-1 shows the absorption of some gases with well-known absorption cross section at a given mixing ratio of 1 ppm.
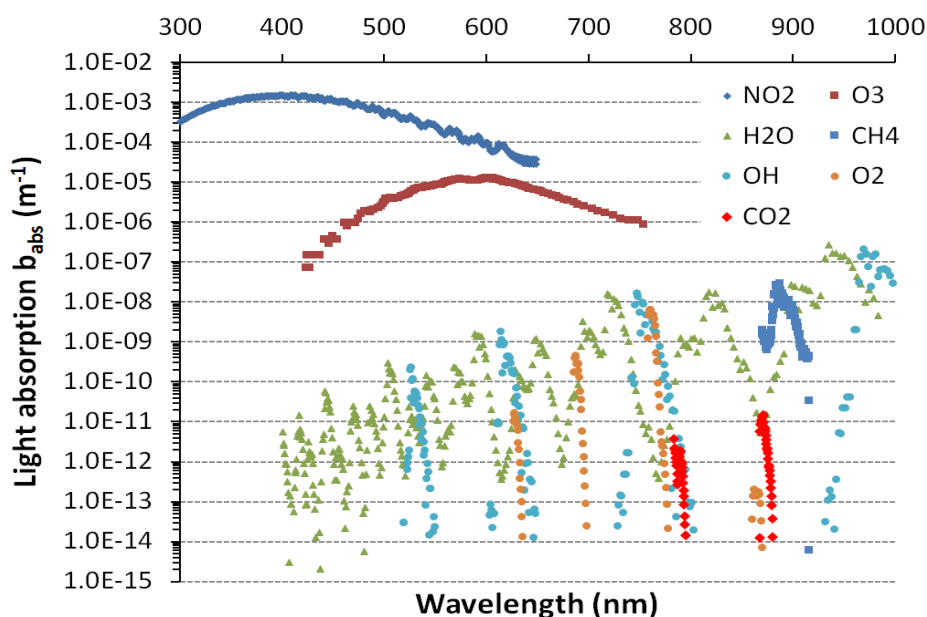
Figure I-1: Wavelength dependence of the light absorption coefficient of various gases with a mixing ratio of 1 ppm. The high-resolution absorption data was taken from the HITRAN database (online access via www.hitran.org) and was smoothed with a Gaussian function to approximate a typical laser bandwidth (5 cm^{-1} filter) used in the photoacoustic and photothermal interferometry systems. If another laser bandwidth is used, the high-resolution data needs to be reintegrated accordingly.

Interference by condensable gas

Volatile components can have an influence on measurement techniques if the measuring system either changes temperature or provides a large surface area, e. g. through fibrous filters.

If the temperature changes, material can evaporate or condensate on particles. The same amount of material can absorb light differently depending on whether it is in the gas or particle phase. A volatile absorbent material, e. g. organic, can lead to a measurement artifact in photoacoustic and photo-thermal interferometry systems, and in extinction cells. In devices with fibre filters, material can be accumulated on the filters and released under changing conditions, such as evaporation with increasing temperature. Artefacts can occur when filters are used as filters to collect the aerosol under investigation or as a part of an automatic baseline correction to produce zero air.

Due to the complex chemistry of aerosol in the field, it is not possible to quantify artefacts of this kind. Therefore, strategies for avoiding artefacts should be investigated. It should be noted that any avoidance strategy could itself change the aerosol and therefore have a direct influence on the absorption coefficient.

Aerosol humidity

Water is a special case of condensable gas as it is omnipresent in the atmosphere. The carrier gas of the aerosol may contain water vapour, which in condensed form can be a significant part of the particle mass. It is recommended that the aerosol be dried when atmospheric measurements are made. For measurements of ambient aerosol, a relative humidity of less than 40 % is recommended by WMO/GAW. Humidity artefacts can occur in all measurements. Therefore, specially designed aerosol dryers are recommended to dry the aerosol before entering any instrument. This is not always done for black carbon instruments, and the effect of incorporating a dryer for these measurements needs to be investigated.

Particle transport losses

Particle transport losses in aerosol pipes are a general problem for all measurement techniques. Particle losses due to diffusion, impaction and sedimentation can be reduced by a suitable design of the aerosol line. Particle transport losses, and associated incorrect measurements of aerosol related parameters can be taken into account by theoretical corrections up to a certain degree.

For correction, the particle number size distribution must be known. With scattering calculations and the assumption of refractive indices, loss corrections for the optical parameters extinction, scattering and absorption can be calculated.

Selection of wavelength

The choice of a suitable wavelength must take several points into account. In addition to the availability of light sources, potential cross sensitivities to absorption by atmospheric gases and the choice of a suitable calibration gas must also be taken into account.

In order to determine BC concentration, wavelengths at which high mineral dust or organic carbon absorption occurs should be avoided. Wavelengths greater than 600 nm are preferred to minimize cross sensitivity to organic carbon and mineral dust.

4.1.3 Methods for measuring aerosol light absorption

Atmospheric light scattering measurements (e.g. with the nephelometer) are precise, straightforward and well established because light scattering can be directly observed and measured in-situ. In addition, these instruments can be calibrated with certain gases having accurately known scattering properties. The measurement of extinction is also a direct method, which theoretically does not require calibration. Devices based on multiple reflectance cells with increased sensitivity (CAPS, Cavity Attenuated Phase Shift) can measure extinction coefficients at atmospheric concentrations. In both cases, the aerosol component needs to be distinguished from the gas component, for example by comparison of results from filtered and unfiltered air. Unfortunately, direct accurate quantitative measurement of atmospheric light absorption is more challenging. In principle, the absorption can be measured as simply the difference between extinction and scattering, but the uncertainties are significant when the absorption is relatively small. Table I-1 gives an overview of existing methods and available instruments for aerosol absorption measurements.

Table I-1: Commercially available in-situ techniques for measuring aerosol absorption, with filter-based techniques for comparison. Since BC is the dominating absorbing species in the atmospheric aerosol, many instruments report BC mass loadings although they estimate the aerosol light absorption coefficient.

Method *Instrument*	Manufacturers	Time resolution	Advantages	Disadvantages	Detection limit [(*)] b_{abs} [Mm^{-1}]	BC mass [ng m^{-3}]
Filter based: *MAAP* *Aethalometer* *TAP/PSAP*	Thermo Scientific Magee Scientific Brechtel/Radiance Research Inc.	A few minutes	High sensitivity, simple, robust	Low accuracy, prone to filter-based artefacts	≈ 0.5	≈ 50
Photoacoustics: Micro Soot Sensor PASS PAX	AVL GmbH DMT, USA DMT, USA	A few seconds	In-situ, fast response, cen be calibrated with absorbing gases	Instruments response is biased by the evaporation of water from light absorbing particles	≈ 50 <10 <10	≈ 5000 <1000 <1000
Laser-induced incandescence: LII SP2	Artium Tech., USA DMT, USA	Real-time	In-situ, single particle analysis (SP2)	Measures refractory BC mass for particles with diamete >70 nm, does not measure absorption	n.a. n.a.	<200 <1 [(+)]
Differential: "Extunction minus scattering"	Various combination	Seconds	In-situ, fast response, cen be calibrated with absorbing	Problematic when aerosol light scattering prevails	≈10	≈1000

(*) for an integration time of a few minutes
[(+)] BC mass of individual particles with D >≈ 70 nm

Filter-based methods

The common method is to collect aerosols on a fibrous filter tape and detect the resulting reduction of light transmittance through the filter. Globally, the most widely used instrument is the aethalometer, produced by Magee Scientific. This filter-based instrument converts the measured reduction of filter light transmittance directly into absorption coefficients and into eBC concentrations. The advantage of filter-based techniques is that they are straightforward, allow for unattended operation, and they are relatively cheap. In addition, they have low detection limits due to the enrichment of the absorbing species on the filter over time: the detection limits can reach 0.05 Mm^{-1} (which corresponds to a few ng/m^3 eBC) when the data is integrated over a sufficiently long time (hours). They also have low interference from atmospheric gas absorption. Unfortunately, these methods have significant drawbacks as they suffer from large particle-property-dependent errors caused by the modification of particle optical properties upon deposition in the filter. Depending on the instrument, the apparent absorption of the filtered aerosol can be up to a factor 5 higher than the corresponding value of the unfiltered (airborne) particles. There are various optical interactions between the deposited particles and the filter medium which can enhance or lower the apparent absorption. One major problem of these methods is the cross sensitivity to scattering material embedded in the filter material which enhances the apparent absorption. This can be caused by other scattering particles but also by semi-volatile gaseous species which condense on the filter and increase the apparent absorption.

The scientific community is well aware of these artefacts and various correction algorithms exist which are based on many assumptions and simplifications. The consequence is that the corrected measurements are still prone to large systematic errors which can amount to ±30-70 %.

Photoacoustic techniques

Instrument principle

Another class of instruments for the determination of aerosol light absorption coefficient is therefore needed which avoids the filter-based artefacts. A better method is to measure the aerosol absorption "directly" with the particles in their natural, suspended state. The common in-situ method makes use of the photoacoustic effect where the aerosol is exposed to modulated laser light in an acoustic resonator. The periodical warming and cooling of the particles and the resulting pressure changes of the carrier gas can be detected with microphones. The optimum pump light frequency (typically a few kHz) is given by the chamber design and is dependent on gas temperature and composition. Even though a few photoacoustic instruments can achieve detection limits of ~0.1 Mm^{-1} (60s), most instruments have considerably higher detection limits. A big advantage of this method is the high time resolution, which allows for emission measurements where e.g. the exhaust gas from internal combustion engines is studied.

Elevated relative humidity

The photoacoustic method encounters a significant bias when measuring hygroscopic aerosols in elevated relative humidity (RH). This is caused by evaporation of particle-bound water from the heated particles, which consume part of the energy as latent heat that would otherwise have contributed to the generation of sound. This phenomenon impairs the investigation of the RH dependence of light absorption using photoacoustics.

Selection of wavelength

The choice of wavelength has to take into account the cross sensitivies of absorbing atmospheric gases and particles as well as the presence of suitable calibration gases. Furthermore, if the measurement is used to estimate the concentration of black carbon, rather than equivalent black carbon, a cross sensitivity of absorption to non-black carbon particles has to be considered.

Photothermal techniques

Instrument principle

The application of photothermal interferometry (PTI) to measure aerosol absorption was demonstrated in the 1990s by researchers in the US: Dr. Moosmüller, Desert Research Institute, and Dr. Sedlacek from Brookhaven National Laboratory.

The sensing part of the PTI instrument developed in this project, is an interferometer for the measurement of extremely small refractive index changes. In this application, an interferometer is used for the measurement of the absorbed energy by aerosols. When particles absorb radiation from an external light source, the absorbed energy is subsequently transferred to the surrounding air. This is done in one of the two branches of the interferometer. As a consequence, the air is heated up, and the gas density around the particle is lowered. This results in a local change of the refractive index of the air which is measured as a change in the phase shift between the two interfering light beams.

Similar to photoacoustics, absorption is directly determined via the measurement of the absorbed energy of a light source. With PTI, the induced temperature change of the air is detected via the change of the refractive index of the air. Calculations have shown that this technique is very sensitive and determines a theoretical detection limit of < 0.01 Mm^{-1} (with a time resolution of about 30 s, dependent on the configuration). However, the practical detection limit of the instrument was shown to be > 0.2 Mm^{-1}. We explain this large discrepancy by the complexity of those PTI prototypes. Indeed, two very thin laser beams (the interferometer laser and the heating pump-laser) must be adjusted such that they overlap over a long distance in order to achieve high sensitivity. In addition, the prototypes are also impeded by the interferometer cross sensitivity to external vibrations.

PTI prototype systems are under development at the FHNW. The current detection limit for both instruments determined by calibration measurements is currently of the order of 400 ng/m³ for 10 second data averaging.

Extinction minus scattering (EMS)

Another way of measuring aerosol light absorption is with differential techniques where both the extinction and the scattering coefficient are measured separately, and the absorption coefficient is obtained as the difference of the two. This works well for highly absorbing aerosols, but the measurement uncertainties increase strongly when the aerosol extinction is dominated by scattering particles, which is commonly encountered in the atmosphere.

The advantages and disadvantages of this method are as follows:

Advantages:

- Scattering coefficients can be measured with integrating nephelometers. Nephelometery is well understood, and instruments are calibrated with gases with known scattering coefficients.
- The calibration of the extinction measurement can be linked to the calibration of the light scattering measurement with 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.

Disadvantages:

- Gas interference can be significant, and the removal of the gas component from the scattering and extinction measurements, for example by comparing filtered and unfiltered air, is not straightforward.
- The difference between values of extinction and scattering can have a high relative uncertainty. The reasons are systematic errors such as gas interference, and noise. Both are significant when having small differences between extinction and scattering coefficients. This leads to a high detection limit for determining absorption coefficients.
- Thorough instrumental design and setup, together with a large amount of experimental effort, are needed to avoid systematic errors.

Scattering measurements (Nephelometry)

Nephelometry is a robust method for measuring the scattering of light by particles. Integrating nephelometers measure the light scattering coefficient of an aerosol. Typically, the measuring cells are closed to prevent ambient light from entering the measuring cell to improve the detection limit. The light scattering coefficient of the aerosol is the sum of the Rayleigh scattering of the carrier gas and the scattering of particles. The instrument is calibrated with a two-point calibration using two span gases, the low span (e.g. particle free air) and the high span gas (e.g. CO_2). However, a correction for device-related errors is necessary, because the scattered light near the scattering angles of 0° and 180° cannot be measured. Historically, these errors are referred to as 'truncation errors'. These errors can be formally described by modifying the angular light intensity function, which would be a sinusoidal function in an optimal instrument.

Although, truncation correction for calibration gases are easy to solve analytically, the correction for particles is fundamentally different, because not all parameters, e.g. particle shape, particle size, chemical composition, internal distribution of the chemical components, are known for exact scattering calculations.

In general, the accuracy of truncation correction is difficult to determine. The investigation of truncation errors and correction procedures is therefore a primary goal.

Manufacturers of devices measuring light scattering coefficients of gases and aerosols have built in Rayleigh scattering coefficients for air and CO_2 in the firmware of their devices. It was found that Rayleigh scattering coefficients of air differ by 1.5 % at 450 nm and the Rayleigh scattering coefficients of CO_2 differ by 0.2 % between Aurora 4000 and TSI 3563 nephelometers. It is necessary to give an overview of literature values and to recommend a standard according to the current state of knowledge. The uncertainty of Rayleigh scattering coefficients and propagation of uncertainties require further investigation.

Extinction measurements with CAPS_{pmex}

Extinction measurements of particulate matter with a CAPS_{pmex} (Cavity attenuated phase shift) suffer from a non-linearity. Furthermore, the effective length of the measuring cell has to be determined experimentally due to the purging air to protect the mirrors. Therefore, the extinction cell must be calibrated against light scattering measurement using non-absorbing particles. This calibration can be performed by comparison measurements with a nephelometer. Nephelometers have been extensively tested in the past, as described above. Therefore, errors are known and can be corrected to a certain extent.

The possibility of CAPS calibration by Rayleigh scattering of suitable gases should also be considered. To ensure comparability between Nephelometer and CAPS, both instruments should be calibrated with the same gases.

Extinction and scattering measurements with CAPS_{pmssa}

A further development of cavity attenuated phase shift techniques is the CAPS_{pmssa}. The extinction measurement is based on the cavity attenuated phase shift techniques as employed in the CAPS_{pmex} particle extinction monitor. Light scattering is measured by incorporating a Lambertian integrating sphere within the sample cell. In contrast to a nephelometer, the contamination of the walls plays an important role. Therefore,

frequent repetition or test of the calibration is necessary. Furthermore, a truncation error must also be considered for this device.

Absorption derived from Extinction and Scattering measurements

Errors both in the measurement of the scattering and the extinction coefficient influence the accuracy of the absorption coefficient. The following list summarizes uncertainties used for error propagation calculations.

- CAPS$_{pmex}$ noise for one minute integration time: 0.2 Mm^{-1}
- Nephelometer noise for one minute integration time: 0.2 Mm^{-1}
- Remaining uncertainty nephelometer after truncation correction: 2 %
- Uncertainty of nephelometer calibration: 3 %

The error of the absorption coefficient calculated according to the rules of error propagation can best be given as a relative error against an extensive property (extinction or absorption coefficient) and as function of the single scattering albedo (see Figure I-2).
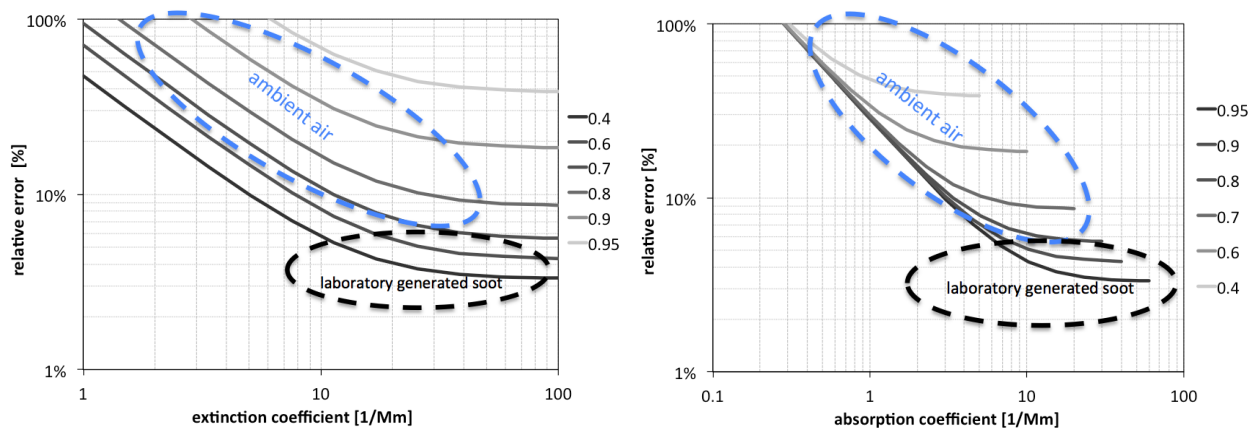

Figure I-2: Performance of Extinction minus Scattering measurements from CAPSpmex and nephelometer. Relative error of derived absorption versus extinction (left figure) and absorption (right figure) for various single scattering albedos.

A similar image for CAPS$_{pmssa}$ cannot be generated at the moment. The reason is that the knowledge of truncation correction is insufficient. For low single scattering albedos, the errors for CAPS$_{pmssa}$ and the CAPS$_{pmex}$ minus Nephelometer combination is expected to be similar.

Humidity effects in EMS

Humidity effects are considered to be low if the relative humidity is below 40 %. With EMS systems, humidity effects have to be taken into account particularly carefully, as the relative humidity can differ between the extinction cell and the nephelometer. A worst case estimation should clarify at which relative humidity and differences in relative humidity between the nephelometer and extinction cell a significant error can to be expected. An estimation can be carried out by using parameterizations of the humidity enhancement factor for different aerosol types. Significant errors are only expected in ambient air measurements with insufficiently dried aerosol.

Particle losses in EMS

In EMS the particle absorption coefficient is calculated by the difference of the measured values from several devices. This method is therefore more vulnerable than other methods to different losses in the aerosol lines to the corresponding instruments. Particle losses are therefore a factor to be taken into account in the design and evaluation of any kind of aerosol measurement. An EMS system with CAPS$_{pmssa}$ reduces the influence of particle transport losses by determining scattering and extinction in the same measuring cell.

4.1.4 Summary

Table I-2 summarises the uncertainties and lists factors that influences the uncertainties. Factors can be caused be technical limitations or due to properties of different aerosols.

Table I-2: Influencing factors on uncertainties of individual instruments.

Extinction minus scattering	
Uncertainty	**Influencing factors**
truncation correction of nephelometer data	- any parameters affecting the particle scattering phase function - particle size - refractive index - particle morphology
nephelometer calibration	- purity of low and high span gases - temperature and pressure compensation - incomplete filling of chamber with calibration gases
CAPS$_{pmex}$ and CAPS$_{pmssa}$ nonlinear response to extinction	- any parameter affecting the baseline level - mirror contamination - misalignment of optical cell due to maintenance or unintentional pressurizing the cell
CAPS$_{pmex}$ and CAPS$_{pmssa}$ effective pathlength	comparison with scattering coefficients of nephelometers including all uncertainties related to nephelometer calibration and correction
truncation correction	- all parameters affecting the scattering phase function - particle size - refractive index - particle morphology - better characterization of scattering geometry needed
CAPS$_{pmssa}$ calibration of scattering channel	- method of calibration (gas or particles) - increasing contamination of optics during measurements
Photoacoustic absorption photometers	
Uncertainty	**Influencing factors**
calibration	- purity of calibration gases - concentration of calibration gas (including temperature and pressure compensation) - uncertainty in laser wavelength
latent heat	volatile material
acoustic signal detection	ambient noise
Photothermal interferometry	
Uncertainty	**Influencing factors**
calibration	- purity of calibration gases - concentration of calibration gases (including temperature and pressure compensation) - uncertainty in laser wavelength
interferometric signal detection	thermal and mechanical stability of interferometer
All methods	
Uncertainty	**Influencing factors**
aerosol transport losses	- particle size - length and bends in aerosol pipes
humidity effects	- aerosol dryers - heating in aerosol pipes inside and outside of instruments

The significance of the individual influencing factors is show in Table I-3. The significance is represented by a ranking between 0 and 3.

Table I-3: Relevance ranking: 0=no relevance, 1=low, 2 medium, 3=high

	EMS (Neph. and CAPS$_{pmex}$)	EMS (Neph. and CAPS$_{pmssa}$)	Filter based	Photo-acoustic	Photothermal interferometry
Aerosol transport losses	2	1	1	1	1
Humidity effects (aerosol hygroscopic growth)	2	1	2	2	2
Scattering measurement: background drift	1	3	n.a.	n.a	n.a
Scattering measurement: truncation	3	3	n.a	n.a	n.a
Scattering measurement: calibration	2		n.a	n.a	n.a
Scattering measurement: air Rayleigh correction	1	1	n.a	n.a	n.a
Contamination of measurement cell	1: Neph. 1: CAPS mirror	3: Integrating sphere 1: CAPS mirror	1	1	1
Gas absorption	2	2	0	2	1
Interference with condensable gases	1-2	1-2	1-2	1-2	1-2
Baseline drift	3	3	1	1	1
Filter effects	0	0	3	0	0

The metrology of light absorption by atmospheric black carbon must take into account the corresponding range of aerosol properties. The relevant aerosol properties here are not those of atmospheric black carbon only, but of the entire aerosol, including interfering gases, non-BC particles, and materials mixed internally with black carbon particles.

The atmospheric-aerosol properties which may affect the determination of aerosol absorption coefficients in the ultraviolet to infrared wavelengths are summarized in Table I-2. In the atmosphere, the variations of these properties indicate the following scenarios.

I. Variations in count median diameter (CMD) reflects BC-particle sources and the mass fraction of non-BC material internally mixed with BC (Fierce et al., 2016).

II. Variations in single scattering albedo (SSA) largely reflect BC mass fraction in the aerosol but are influenced by internal mixing (mass fraction of BC in a BC-containing particle).

III. Variations in mass absorption coefficient (MAC) reflect the BC-particle source and mixing state.

IV. Variations in BC concentration reflect source strengths, dilution, and surface deposition.

V. Variations in morphology are caused by internal mixing.

A method to measure atmospheric BC concentrations will ideally be insensitive to the variation of the properties listed in Table I-4. To evaluate this sensitivity, the laboratory characterization of such a method should include variations in these listed properties. For example, the CMD of a test aerosol can be varied by using aerosol classifiers (by differential mobility with a DMA, or by aerodynamics with an AAC). The SSA can be varied by external mixing with non-absorbing aerosols, or by internal mixing. For the internal-mixing case, single-particle-mass measurements are then necessary to quantify the degree of internal mixing. The project successfully achieved the objective with these results. The work for the objective was led by TROPOS, with contributions from PTB, NPL, IL, METAS, LNE, PSI, FHNW and NCSR Demokritos. .

Table I-4. Aerosol properties of BC-containing aerosol relevant to absorption-coefficient measurements, as found in the atmosphere (second column) and as produced in the laboratory. CMD: count median diameter. SSA: single-scattering albedo. t.b.d.: to be determined (more data needed). MAC: mass absorption coefficient. eBC: mass concentration of black carbon equivalent to a measured absorption coefficient.

Property of BC-containing aerosol	Atmosphere	Flame source	Nebulized CB	Nebulized PSL (monodisperse)	Spark generation
CMD	50-400 (BC-contain-ing particles only) 50-800 (all)	50-300, MAE covaries	30-500	50-800	50-150
SSA (550 nm)	0.2$^{(*)}$ – 1.0	0.2 – 0.6	0.2	t.b.d.	0.2 – 0.3
MAC(λ) [m^2/g]	7.5 – 12 (550 nm)	0.1 – 5.5 (550 nm)	t.b.d.	t.b.d.	5.7 (450 nm)
Max abs. coeff. [1/Mm at 880 nm]	0 to ~500	t.b.d.	t.b.d.	t.b.d.	t.b.d.
Max Conc. [μg eBC/m^3 at 880 nm]	0.01 to ~100	>1E+05	moderate (t.b.d.)	low (t.b.d.)	high (t.b.d.)
Morphology	fractal-like to compact	fractal-like	partly fractal-like	spherical	fractal-like

$^{(*)}$ Lowest value of 0.2 can be found for fractal particles near traffic emissions.

4.2 Objective 2: Black carbon Standard Reference Materials
4.2.1 Introduction

The aim of this objective was to develope and tested different methods used to generate light absorbing aerosol particles that can potentially be used for field calibration of light absorption measurement instruments. A 'golden generator', suitable for BC absorption field calibrations, would need to provide a stable source of aerosol particles with a reproducible geometric mean diameter and geometric standard deviation, and a stable single scattering albedo. Ideally, the aerosol should have a stable and well characterised fractal dimension, mass-specific absorption cross section and absorption Angstrom exponent, in the near-UV visible range. Ideally, the calibration process should involve several different controlled-property aerosols that span the range of particle properties likely to be encountered in the field. For practical considerations, the project aimed to use two types of calibration aerosol. Thus two distinct kinds of SRM aerosol were proposed; one resembling fresh soot and another one resembling aged and coated soot particles. Any field instrument would need to give satisfactory measurements for both types of particle.

4.2.2 Relevant properties of SRMs and techniques for generation

Desirable properties of the aerosol

The controlled properties of the calibration aerosol must include the following:

- Absorption coefficient at the chosen wavelength (Mm^{-1}) – the metric being calibrated
- Particle size – mean size, and width of size distribution (nm) – to simulate the penetration of ambient particles into the filter used by the instrument
- Single scattering albedo (SSA, the ratio of scattering efficiency to extinction efficiency – a dimensionless quantity) – to simulate the loading and scattering effects of ambient particles within the filter.

The latter two properties represent the move away from the original "near-black carbon" idea. Particle size specification is necessary to control penetration into the filter, whereas if the filter was not a factor, the particle size would not matter, only the absorption coefficient. A "near-black carbon" source would have as low an SSA

as possible, whereas a more representative calibration source will have an SSA closer to those found for ambient air particles.

No specification was made on the morphology of the particles, although this is also of interest, for example because it affects the determination of the particle size. Carbonaceous material from combustion processes is morphologically regarded as a fractal-like structure with primary particles with a graphitic or amorphous structure. The number and size of the primary particles and their arrangement, which is described by the fractal dimension, are the common sizes for description. The morphology of a particle with a non-negligible amount of organic carbon is more difficult to describe. With a small amount of organic carbon, a thin layer can coat the primary particles. In a larger proportion, a fractal of black carbon may be completely enclosed in an organic drop. In addition, the arrangement of the primary particles may also change.

A simple measure of the chemical composition of particles is given by the ratio EC (elementary carbon) to TC (total carbon), as determined by the standard thermo-optical method (EN 16909:2017). Elemental carbon is often equated to black carbon, but this is not an exact relationship because the two substances are defined by different measurement techniques. Organic carbon consists of a large number of substances and can vary greatly in composition between different carbonaceous materials. In effect, the EC/TC ratio gives an indication of "black" carbonaceous material relative to "non-black" carbonaceous material, which is loosely connected to the particles' SSA, which is a measure of scattering (non-absorbing) material relative to absorbing material, described below.

The SRMs were described as being similar to (1) freshly emitted combustion particles and (2) aged combustion particles respectively, and characterized as (1) size 50 - 100 nm, Single Scattering Albedo (SSA) 0.05 – 0.2 at 550 nm, and (2) size 200 - 400 nm, SSA 0.7 – 0.9 at 550 nm.

Potential generators for SRMs

Diffusion flame mini-CAST

The mini-CAST (Jing Ltd., Zollikofen, Switzerland) is a propane co-flow diffusion flame soot generator. The aerosol stream is mixed with nitrogen, used as quenching gas, to prevent further combustion processes and to avoid condensation. The stream is then diluted with compressed air. Particle size, composition and number concentration can be tuned by changing different operating parameters like dilution air, mixing nitrogen (to dilute the fuel), and changing the fuel-to-air ratio in the flame. The latter one is usually expressed as ϕ, which has a value of 1.0 for stoichiometric combustion. A $\phi > 1$ corresponds to fuel-rich conditions, whereas a $\phi < 1$ corresponds to fuel-lean conditions.

Different diffusion flame mini-CAST models were used during the experiments presented here, including two mini-CAST 5203C (TROPOS and PTB) and a mid-mass mini-CAST 5303C, provided by Jing Ltd.

Pre-mixed flame mini-CAST

The mini-CAST 5201 Type BC (Jing Ltd., Zollikofen, Switzerland), hereafter referred to simply as mini-CAST BC, was used as an aerosol generator. It was operated with a partially premixed flame [1], where mixing air is directly added in the propane flow to achieve premixed flame conditions. Since the flame is still surrounded by oxidation air, which is needed for stabilizing the flame, the latter is not a purely premixed but rather a combination of a premixed and a diffusion flame. As in other mini-CAST models the flame is quenched with a nitrogen flow. The mini-CAST was always operated at near-stoichiometric but overall slightly fuel-lean conditions.

Miniature inverted soot generator

This generator consists of a co-flow inverted diffusion flame. It can be operated using ethylene or propane as fuel. Air and fuel flow rates can be changed to produce fuel-rich or fuel-lean combustion and particles with different size, which vary from 85 to 200 nm diameter. The device used during the workshop is manufactured by Argonaut Scientific Corporation (Edmonton, Canada).

Nebulisation

For nebulised aerosol experiments a portable reference aerosol generator (PRAG) system provided by LNE was used. It is composed of a clean-air tank connected to a constant output atomizer (model 3076, TSI, USA). A diffusion dryer (model 3062, TSI) is used downstream of the atomizer outlet to remove water from the particles (relative humidity of around 95 % and 50 % before and after drying, respectively) and a four-way valve allows coupling with instruments. The PRAG system is a combination of commercially available components with minor technical modifications made to reinforce its robustness for transport. Considering the desirability for air quality monitoring networks of a portable generator for field calibration, this system could

provide to an easily portable generator due to its light weight, and it also constitutes a self-governing system without need of an electrical source.

The types of particle nebulized were:

I.   Aquadag® (colloidal graphite)

Aquadag® (Aqueous Deflocculated Acheson Graphite) from Acheson Inc., USA is a colloidal dispersion of aggregates of irregular flakes of in water (80 % H_2O as delivered).

II.   Fullerene soot

Fullerene soot particles are fractal-like aggregates of spherical primary particles with a diameter of 50 nm and they are composed of 90 % amorphous carbon (carbon black) and 10 % fullerenes (mainly C60).

III.   Black-dyed PSL

Black-dyed polystyrene latex (PSL) particles (Polysciences Europe GmbH, Polybead Polystyrene Black Dyed Microspheres) are provided at a size of 200 nm. However, experiments with these particles at TROPOS failed and would need to be redone with higher particle concentrations.

Spark discharge generators

The basic components of the spark discharge source are the chamber, which houses two opposing graphite electrodes, mounted at an adjustable distance, forming a gap of up to a few millimeters. The source is connected to a carrier inert gas of high-purity. The electrodes are connected to a high voltage supply, in parallel to a capacitor. The spark discharge generator produces aerosol particles by ablation of carbon from two opposing graphite electrodes via spark discharge in the inert atmosphere. The evaporated material cools down rapidly after the discharge and particles are formed by condensation and aggregation. The particle size and mass concentration of the produced nanoparticles can vary by adjusting the carrier gas flow rate, the spark energy and the spark frequency.

In the experiments presented here two different spark generators were used:

- GFG 1000 (Palas GmbH, Karlsruhe, Germany), operated with argon (4.8 purity) as the carrier gas.
- Fasmatech spark generator (Fasmatech Science and Technology SA, Athens, Greece) operated with nitrogen (5.0 purity) as the carrier gas.

Catalytic Stripper / thermodenuder

Catalytic Stripper model CS015 (Catalytic Instruments, Rosenheim, Germany) operated at 150 and 350 °C and a flow rate of 1.5 l/min.

4.2.3 Experimental details of the laboratory tests and intercomparison workshops

PTB: miniCAST, fresh soot

A mini-CAST 5203C was used to produce fresh-like soot particles that were treated with a Catalytic Stripper at different temperatures (see Figure II-1). The aim of the experiment was to study aerosol optical properties and particle size distributions of particles produced at different fuel-to-air ratios (from fuel-lean to fuel-rich conditions), and treated at different temperatures in the volatile particle removal (VPR) system (150 °C and 350 °C). Non-treated particles were also studied by passing the particles through a bypass line at room temperature (21 °C, no VPR treatment).
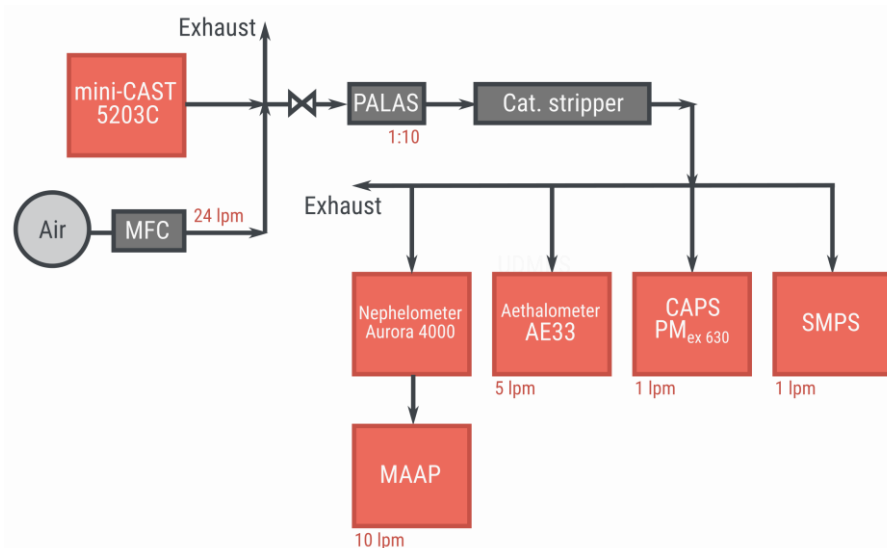
Figure II-1: Schematic diagram of the instrumental setup for the PTB experiments. The 2nd dilution step (PALAS 1:10) was performed prior to the Catalytic Stripper.

The aerosol output was analysed by different instruments to measure optical properties: scattering coefficients were measured by a nephelometer (Aurora 4000, Ecotech, Australia), absorption coefficients were measured at 647 nm by a MAAP (Thermo Scientific, USA) and at 7 different wavelengths by an Aethalometer (AE33, Magee Scientific, USA), extinction coefficients were measured at 635 nm by a CAPS$_{pmex}$ (Aerodyne Research, USA). Aerosol mobility size distributions were measured by a SMPS (TROPOS).

METAS

Fresh soot (METAS 1)

The mini-CAST 5201 Type BC (Jing Ltd., Zollikofen, Switzerland), hereafter referred to simply as mini-CAST BC, was used as aerosol generator. It was operated with a partially premixed flame, where mixing air is directly added in the propane flow to achieve premixed flame conditions. Since the flame is still surrounded by oxidation air, which is needed for stabilizing the flame, the latter is not a purely premixed but rather a combination of a premixed and a diffusion flame. As in other mini-CAST models the flame is quenched with a nitrogen flow. The mini-CAST was always operated at near-stoichiometric but overall slightly fuel-lean conditions.

The aerosol sampled at the outlet of the mini-CAST's exhaust pipe was guided through a diffusion dryer filled with silica gel and diluted by a rotation disc diluter. The particles were analysed with an SMPS, TEOM, PAX and Aethalometer or sampled on filters or TEM grids for subsequent analysis as shown in Figure II-2.
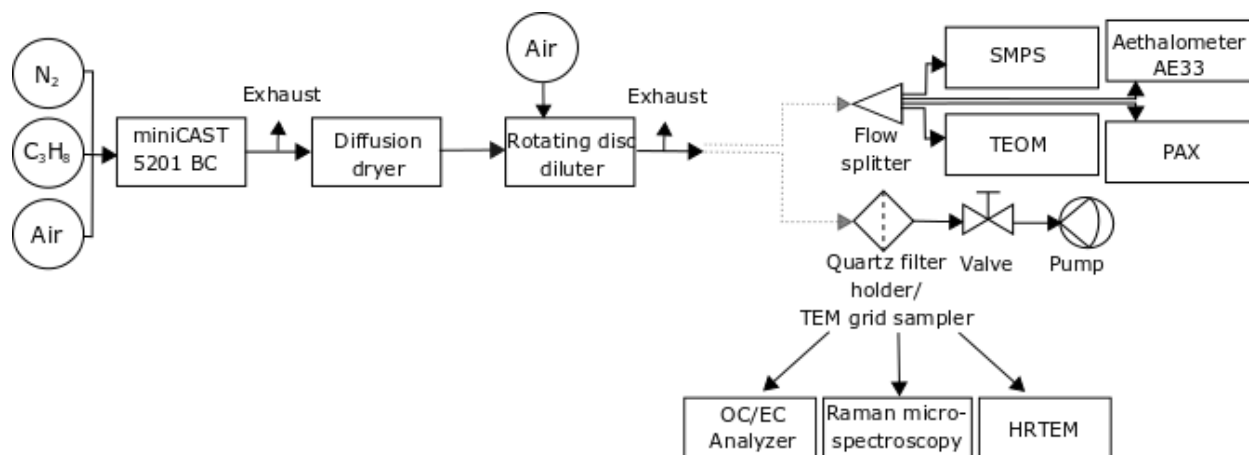

Figure II-2: Schematic illustration of the setups for the characterization of the mini-CAST BC soot.

The particle size distribution was determined with an SMPS in stepping mode. The aerosol mass concentration was measured with a TEOM 1405, which was operated with a main flow rate of 1 L/min at 30 °C. A PAX was used to determine the SSA and the absorption coefficient at 870 nm, while an Aethalometer AE33 was used to calculate the Ångström absorption exponent AAC (from all wavelengths).

Filter samples were collected for EC/OC analysis, Raman microspectroscopy and (High Resolution) Transmission Electron Microscopy (TEM/HRTEM). For the EC/OC analysis and the Raman measurements, the aerosol was sampled on quartz fibre filters. To collect the particles on TEM grids, a tandem DMA setup was used in combination with a mini particle sampler. The EUSAAR2-protocol (Cavalli et al. 2010) used to determine the composition with an OC/EC Analyzer was modified by extending the last temperature step (850 °C) from 80 s in the original protocol to 120 s in order to ensure complete evolution of carbon. Raman microspectroscopy was performed with an upright Raman microscope (ND-MDT NTEGRA Raman microscope) equipped with a laser of 532 nm wavelength and a 50✕ objective lens. After background correction of the spectra, the spectra were normalized to the graphitic G-Peak at about 1600 cm^{-1} and averaged to yield one mean spectrum for every operation condition. The peak ratio of the two Raman soot peaks I(D)/I(G) was determined from the spectra. Results from Raman analysis are not shown in this report.

Aged soot (METAS 2)

The mini-CAST was operated in the "premixed flame mode" under overall slightly fuel lean conditions in order to maximize the EC/TC (elemental carbon EC to total carbon TC) mass fraction of the soot particles. After drying, the aerosol was diluted at 1:10 ratio with dry particle-free air (VKL 10 dilution unit, Palas GmbH, Germany), which resulted in ≤5.5 % relative humidity (RH). The aerosol humidity was measured right before the MSC with a digital humidity sensor (FHAD 46 series/Almemo D6, Ahlborn, Germany).

The soot particles were then mixed in the micro smog chamber (MSC, model with 2 quartz tubes) with α-pinene (≥97 % purity, Sigma Aldrich, Switzerland) which served as the volatile organic compound VOC. The α-pinene concentration in the soot- α-pinene-mixture was controlled by adjusting the flow of zero-air through the α-pinene container with the use of a mass flow controller (MFC, Vögtlin, Switzerland) and was determined with a photoionization detector (PID PhoCheck TIGER, Ion Science Ltd, UK) after filtering out the particles as shown in Figure II-3.. In the MSC, the α-pinene vapours were oxidized by O$_3$ generated with UV-light, yielding secondary organic matter (SOM), part of which deposited on the soot particles as coating.
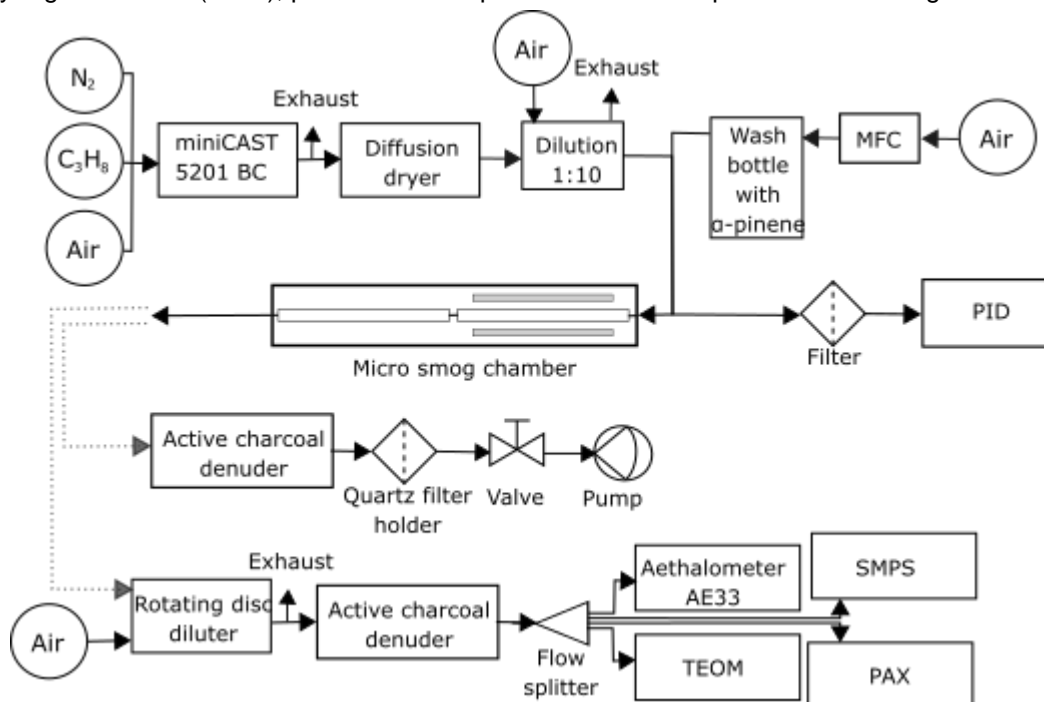

Figure II-3: Schematic diagram of the instrumental setup for the METAS soot coating experiments.

The processed (coated) aerosol was diluted with a rotating disc diluter (Matter Engineering, Switzerland) placed right after the MSC. After passing through a denuder filled with activated charcoal to (partly) remove the gas phase organics, the aerosol was split and delivered to a scanning mobility particle sizer (SMPS 4.500,

Grimm Aerosol Technik GmbH & Co. KG, Germany, L-DMA, Am-241 neutralizer), an Aethalometer (AE33 Aethalometer, Magee Scientific, USA), a photoacoustic extinctiometer (PAX, 870 nm wavelength, Droplet Measurement Technologies, USA) and a tapered element oscillating microbalance (TEOM 1405, Thermo Scientific, USA), respectively. Alternatively, the aerosol was sampled undiluted on quartz fibre filters (Advantec, Japan, QR-100, 47 mm, prebaked at 550 °C for 1.5 h) at a flow rate of 1.2 L/min after passing through a denuder filled with activated charcoal. The particle loaded quartz fibre filters were later analysed with a thermal-optical method (Lab OC-EC Aerosol Analyzer, Sunset Laboratory Inc., USA) using the EUSAAR_2 protocol with an extended last temperature step.

TROPOS: generator intercomparison workshop

Different generators provided by the consortium were brought to the aerosol laboratories at TROPOS (Leipzig, Germany) to perform a comprehensive comparison by measuring optical properties, particle size distribution, EC/TC ratio, and Raman spectra (see Figure II-4).
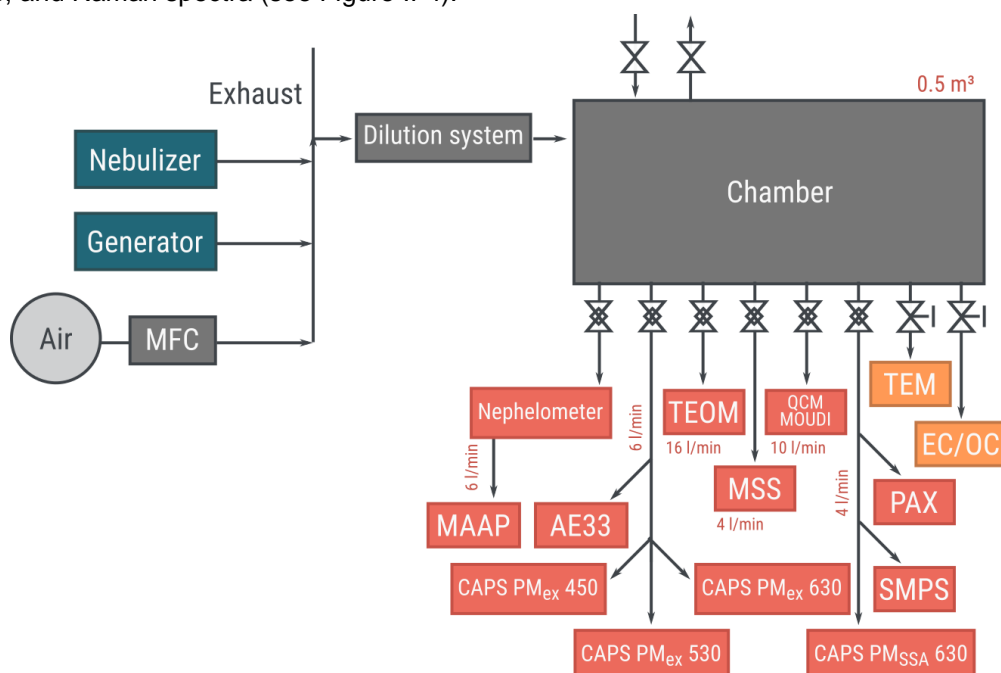

Figure II-4: Schematic diagram of the instrumental setup for the TROPOS generator intercomparison workshop.

The generated aerosol particles were diluted with dry particle-free air and fed to a 0.5 m³ chamber at low relative humidity. The aerosol was then analyzed by several online instruments including three CAPS$_{pmex}$ (450, 530, 630 nm, Aerodyne Research, USA), one CAPSSSA (630 nm, Aerodyne Research, USA), a MAAP (637 nm, Thermo Scientific, USA), an Aethalometer (7 wavelengths AE33, Magee Scientific, USA), a micro-soot sensor (MSS, AVL, Austria), a PAX (870 nm, Droplet Measurement Technologies, USA), a nephelometer (Aurora 4000, Ecotech, Australia), an SMPS (TROPOS, Germany), a TEOM (model 1405, Thermo Scientific, USA), and a Quartz Crystal Microbalance (QCM) MOUDI (Thermo Scientific, USA). Passive samplers were used to collect samples for TEM, EC/OC analysis and Raman microspectroscopy. Instruments were provided, operated and their data processed by members of the consortium, PTB, NPL, TROPOS, METAS, LNE, PSI, FHNW, NCSR Demokritos and IL. .

NRC: characterisation of inverted flame burner

Some characterization of the inverted flame burner used in the TROPOS intercomparison was carried out at NRC Canada. The concentration of EC increased with ethylene flow rate while the concentration of OC was comparatively small, leading to high ratios of elemental to total carbon at high ethylene flow rates. Transmission electron microscopy images of soot particles from the flame showed that the majority of soot particles were sub-micron in size and had aggregate structure. Large clustered super aggregates, typically larger than 2 mm, were observed for all studied samples, and their abundance increased with ethylene flow rate. Thus, if users wish to use the burner as a source of soot nano particles, then high fuel flow rates should be avoided or large super aggregates could be removed using an impactor or a cyclone.

4.2.4 Results

Data from the experiments presented above are summarized here. Not all parameters were measured in all experiments. However, there are some overlaps between the experiments which are presented here.

The particle size distribution was given in some experiments with the number mean. If possible, the volume mean was given in addition to the number mean. A conversion of the mobility diameter into volume equivalent diameters under consideration of the morphology was not carried out. The calculation is based on the assumption of spherical particles.

In this summary the focus is on the single scattering albedo (SSA), Ångström absorption exponent (AAC), mass absorption coefficient (MAC) and EC/TC (Figure II-5, II-6, II-7).
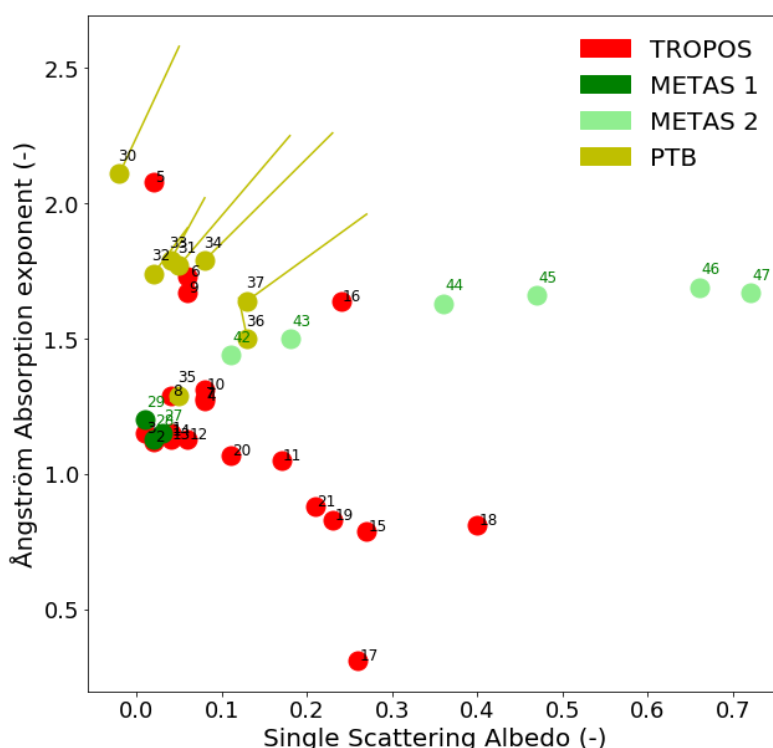

Figure II-5: Ångström exponent compared to the single scattering albedo. The numbers at the points refer to the number of the experiment. For PTB, the change of the properties by the removal of the organic material is represented by a line. The endpoint shows the properties after treatment with the Catalytic Stripper. Note, that single scattering albedos are determined for different wavelengths (PTB 635 nm, TROPOS and METAS 870 nm).
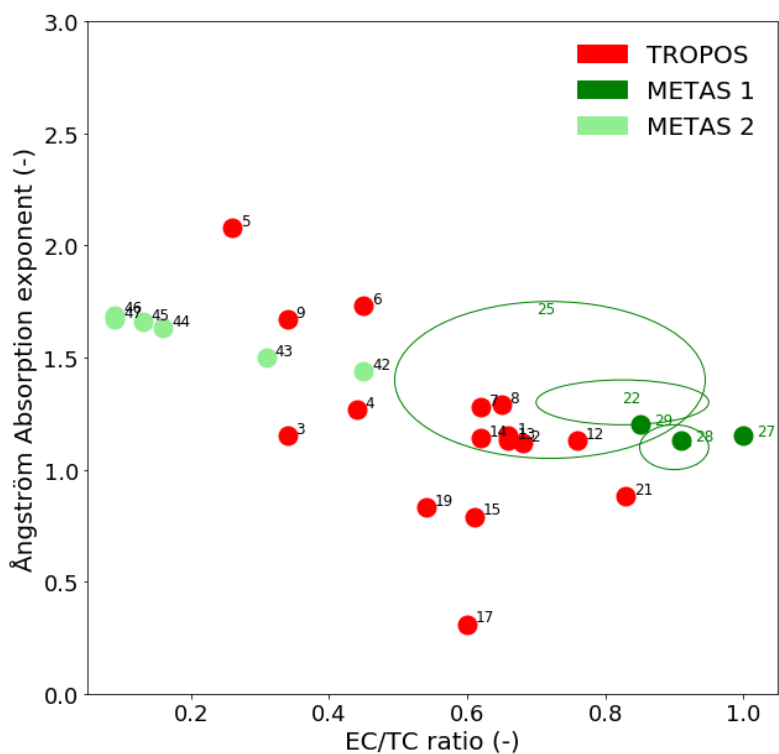
Figure II-6: Ångström exponent compared to EC/TC ratio. The numbers at the points refer to the number of the experiment. For METAS, the possible value ranges were represented by the ellipses. This representation is only very rough.
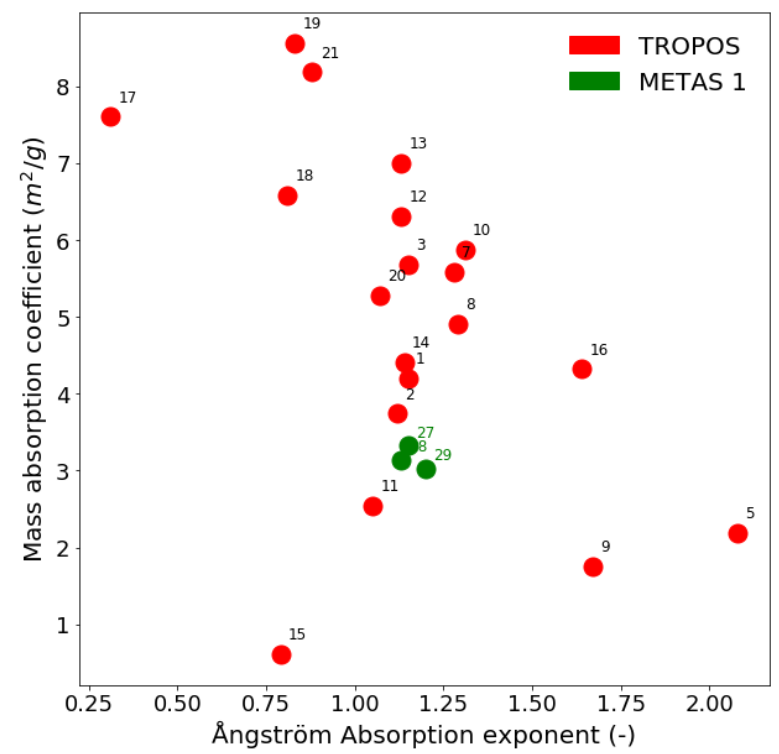

Figure II-7: Mass absorption coefficients compared to Absorption Ångström exponents. The numbers at the points refer to the number of the experiment.

4.2.5 Summary and Recommendations

The calibration of field BC monitoring instruments (filter absorption photometers) with aerosols that can be generated reproducibly and are relevant for ambient air monitoring requires knowledge of how sensitive the instruments are to different aerosol properties. To our knowledge, no systematic investigation with soot particles of varied properties for other types of instrument has yet taken place. For this reason, MAAP and AE33 were included in the TROPOS measurements. Figure II-8 shows the ratio of the absorption coefficients of MAAP and AE33 to the reference system. There is clearly a size dependence. However, the other variable properties of the aerosols of different generators seem to have relatively little effect as the variance is quite low. This observation needs to be investigated further with a comprehensive error analysis. We suspect that main observation is linked to the size-dependent penetration depth of the particles in the filter material. From this we could deduce that the most important parameter to control for the two aerosol particle types used to calibrate field monitors is the particle size. Table II-1 gives an overview of the reference materials tested.
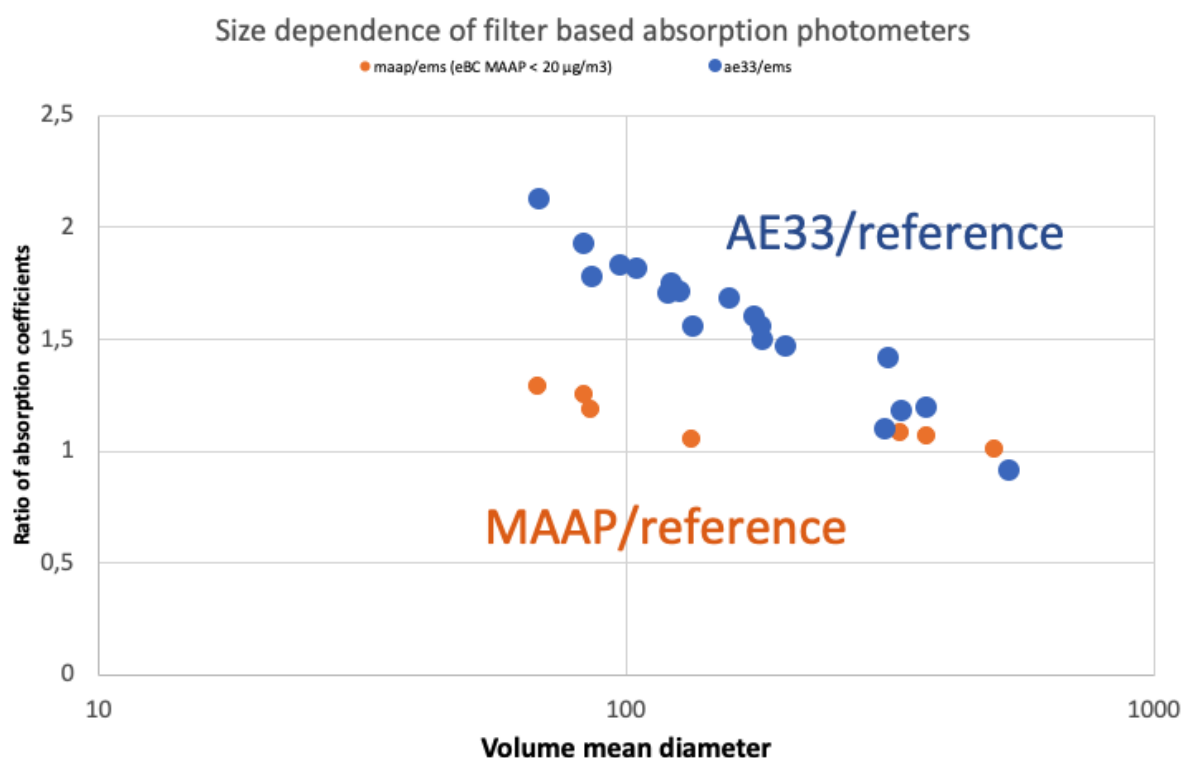

Figure II-8: Ratio of absorption coefficients from MAAP and AE33 to the reference (EMS) as function of the particles volume mean diameter (in nanometres).

Table II-1: Summary of properties of potential reference generators.

Generator type	Generation effort	Repeatability /stability	Particle size distribution	Single scattering albedo (870 nm)	Ångström Absorption exponent
mini-CAST	large, requires technical gases and dilution system	individual operating points must be elaborated for individual generator	can be controlled between 20 and about 130 nm; high EC/TC mass fraction just for the larger particles	variable depending on operating point, <0.2	variable depending on operating point, between 1 and 2
mini-CAST BC	large, requires technical gases and dilution system	very good stability; repeatability better than 6 % in particle size and 10 % in number concentration	particle with high EC/TC mass fraction in large size range (50 - 200 nm)	<0.02 for high EC/TC ratio	1.0 to 1.4
mini-CAST BC + MSC	large (c.f. mini-CAST) plus additional micro smog chamber (MSC)	see mini-CAST BC, MSC needs further charact-erization	up to 200 with coating (further characterization required)	0.1 to 0.7 depending on coating	1.4 to 1.7 depending on coating
Inverted flame	Large, requires technical gases and dilution system	Repeatability within 6-30 % in particle size	can be varied down to 85 nm, but less reliable below 100 nm	≈ 0.2	≈0.8 to 1.1
Black-dyed PSL	small, requires nebulizer and aerosol drying	excellent	well defined	no information due to low signal at TROPOS	no information due to low signal at TROPOS
Aquadag	small, requires nebulizer and aerosol drying	low variability between different charges	bimodal for operating points at TROPOS, VMD rather large (≈315 nm)	≈0.3	≈0.3
Fullerene soot	small, requires nebulizer and aerosol drying	Poor	Bimodal at TROPOS VMD rather large (≈330 nm)	≈0.4	≈0.8
Spark generator	large, requires technical gases and dilution system	Depending on model	size distribution variable depending on operating point	≈0.2 to 0.3	≈0.8 to 1.6

Some more specific observations that should be considered are:

- Generators of the mini-CAST type have shown good stability in laboratory tests. However, it is necessary to find the desired operating parameters (or working point) for each generator by pre-testing. The transport of a mini-CAST BC from METAS to TROPOS and back to METAS showed that the working points had shifted. Fluctuations in the total pressure in the combustion chamber have an influence on the flame and the properties of the soot produced. Therefore, operating points only keep their validity if the dilution section is also considered as part of the overall system. At METAS it was also observed that the purity of propane influences the working point (personal communication K. Vasilatou).

- Black-dyed PSL particles could not be measured at TROPOS due to contamination. The original sample from the LNE shows no contamination (personal communication F. Gaie-Levrel). The contamination is only visible if the volume distribution is plotted. Possible contaminations are difficult to identify from number size distribution measurements.

Absorption measurement systems are based on different methods. Differences between the methods are greater than differences between devices of the same type because different properties are measured. In order to use instruments in the laboratory or in the field, they must therefore meet certain conditions. These can be specified with the technical data such as detection limit, time resolution, systematic errors, cross sensitivities. For reference measuring instruments in the field, other information such as portability, stability and possibilities for calibration are also important. These properties are compared for potential reference instruments in Table II-2. Factors influencing the application of methods as reference systems are given in Table II-3.

Table II-2: Properties of field monitors and potential reference systems.

Method Instrument	Time resolution	Advantages	Disadvantages	Detection limit (*)	
				b_{abs} [Mm^{-1}]	BC mass [ng m^{-3}]
Filter based: MAAP (Thermo) Aethalometer(Maggee) TAP/PSAP (Brechtel/Radiance Reserach)	minutes	High sensitivity, simple, robust	low accuracy, prone to filter-based artefacts (multiple scattering, apparent absorption by scattering particles)	≈ 0.5	≈ 50
Photoacoustics: e.g. Micro Soot Sensor (AVL), PASS (DMT), PAX (DMT)	a few seconds	In-situ, fast response, can be calibrated with absorbing gases	Instruments response is biased by the evaporation of water from light absorbing particles, potential gas absorption depending on wavelength	<10 to 50	<1000 to 5000
Extinction minus scattering (CAPS_pmex and Aurora4000 instruments)	minute	In-situ, fast response, can be calibrated Rayleigh scattering gases	for high single scattering albedos the detection limit increases	≈10	≈1000
PTI (Photothermal interferometry)	10 seconds	In-situ, fast response, not sensitive to scattering, can be calibrated Rayleigh scattering gases	Cross sensitive to external vibrations and acoustic noise	≈3	≈400

Table II-3: Factors influencing the application of methods as reference systems.

Instrument	EMS (extinction minus scattering)	PAX	CAPS$_{ssa}$	PTI (under development)
Principle	Extinction and scattering measured in separate instruments	Photoacoustic photometer and inverse nephelometry	Extinction and scattering measured in single cell	Photothermal effect
primary measurands	extinction coeff., scattering coeff.	absorption coefficient and scattering coefficient	extinction coeff. and scattering coeff.	absorption coefficient
calibration	calibration with certified Rayleigh scattering gas; cross calibration between instruments with non-absorbing aerosol	calibration with aerosols (calibration bound to internal extinction cell); systematic investigation of calibration with different aerosols missing	extinction needs to be calibrated, cross calibration between scattering and extinction	with certified absorbing gas
portability	high transportation effort, requires full calibration after transportation	good	good	to be tested
full traceability	yes	no	no, calibration with certified gases to our knowledge not reliable	under investigation
derived measurands	absorption coeff. Ångström exponent for multi wavelength	single scattering albedo	absorption coeff. and single scattering albedo	-
single/multi-wavelength	single or multiwavelength	three wavelength instrument available	single	single
applicability in field as absorption reference for ambient aerosols	high detection limit requires very high aerosol concentrations	detection limit sufficient	high detection limit requires high aerosol concentrations	detection limit at medium/ high concentration sufficient (to be tested)
applicability as primary or secondary reference for generated soot	primary standard in laboratory	secondary standard in laboratory and field	secondary standard in laboratory and filed	primary or secondary standard (traceability under investigation)

The results provided a clear way forward for the two types of calibration aerosol source required by the project. There are several possibilities for the "fresh" combustion aerosol (size 50 - 100 nm, SSA 0.05 – 0.2), and some of these may be suitable for calibrations in the field. For the "aged" combustion aerosol (size 200 - 400 nm,

SSA 0.7 – 0.9), the MiniCAST BC + MSC produces the required particles reproducibly. It is not possible to be taken into the field for calibration at sites, but it is suitable for calibration within a laboratory, which still meets the agreed objectives of the project.

The way to field measurements with a fully traceable calibration chain is outlined below. It will be possible or even necessary for the user to deviate from the suggestions under justified circumstances. The following outline is proposed to take into account the characteristics of the generators and reference instruments shown in Tables II-1, II-2 and II-3 [1]:

1) The best possible generators of calibration aerosols, in terms of particle size and single scattered albedo, are selected after further experimental work.

2) In the laboratory, a secondary absorption reference instrument is calibrated against a traceable primary absorption reference system using the aerosol generators from 1).

3) The secondary absorption measurement from 2) and the generators from 1) are used in the field to calibrate monitoring instruments. It should be noted that, although the secondary reference instrument provides a check on the stability of the aerosol generators, a minimum degree of stability will be necessary.

4) Alternatively, field instruments can be calibrated in the laboratory using the generators from 1) and either primary of secondary reference systems.

5) Optionally, further measurements in the laboratory and in the field can be used to control the aerosol properties. These are e.g. a particle size spectrometer (SMPS/DMPS) to control the particle size of the calibration aerosol, or a measurement of the spectral absorption to control the EC/TC ratio. Although a multi-wavelength Aethalometer (AE31 or AE33) should initially be considered "uncalibrated", the spectral response of the absorption can be used as a check.

The project successfully achieved the objective with these results. The work for the objective was led by PTB, with contributions from consortium members, NPL, TROPOS, METAS, LNE, PSI, FHNW, NCSR Demokritos and IL. .

4.3 Objective 3: A traceable, primary method for determining aerosol absorption coefficients

4.3.1 Introduction

The aim of this objective was to establish SI traceability for black carbon measurements. Specifically, this means to develop a traceable, primary method for determining aerosol absorption coefficients, using particulate black carbon (BC), at specific wavelengths. Methods need to be suitable both for calibrating instruments in the laboratory, or if possible in the field, and for certifying the properties of the Standard Reference Materials of Objective 2. Two potential Si-traceable primary methods were identified. These are the well-known EMS method, based on a combination of nephelometer and extinction cell, and the PTI technique.

4.3.2 Measurement techniques

Extinction minus scattering: Combination of CAPS$_{pmex}$ and Nephelometer

Measurement setup

The setup consists of a three-wavelength nephelometer Aurora4000 (Ecotech Pty LTD , Australia) and three CAPS$_{pmex}$ (Aerodyne Research, Inc., USA) devices. The wavelengths are 450 nm, 525 nm and 635 nm for the nephelometer and 450, 525, 630 nm for the respective CAPSpmex. Due to the design with a total of four separate cells for measuring scattering and extinction, care was taken to minimise particle transport losses to all instruments and, very important, to ensure that the losses are similar. Since different losses can occur especially for coarse mode particles, it is recommended to use a pre-separator (PM$_1$).

Instrument corrections and calibration

To determine the light absorption coefficient, the instruments must be calibrated and the values corrected. First, the necessary corrections are introduced, as these are also essential for calibration.

Integrating nephelometers measure a value close to the true light scattering coefficient. However, due to the construction of the detector, only a scattering angle range of 7° to 170° is covered and the light source does not correspond to an ideal Lambertian light source as required by theory. It must be emphasized, that the truncation error increases with increasing particle size and its correction also becomes more uncertain. The baseline value of a Nephelometer is subject to drift which must be corrected by repeated baseline

measurements. It has been found that under optimal conditions, i.e. stable temperatures and low aerosol humidity, it is sufficient to measure the baseline once a day.

The CAPS$_{pmex}$ method requires the exact light path length in the measuring cell. However, the ends of the cell are highly reflective mirrors and must be protected from contamination by a purge air flow. The purge air shortens the effective light path length slightly and dilutes the sample aerosol. To correct this, a light pathlength factor must be introduced, which should be determined for each unit. The baseline of a CAPS$_{pmex}$ is subject to drift. Since the baseline drifts much more in comparison to a Nephelometer, it must be measured more frequently. Periods between 5 and 15 minutes have proven to be practical. Since a baseline measurement takes up to 2 minutes, the loss of data seems to be very high. However, for the calculation of the absorption from the difference of extinction and scattering, the data quality is very important and the loss of data during the baseline periods has to be accepted. Furthermore, a numerical method to improve the quality of the baseline correction was published [4]. The absorbance measured with CAPS$_{pmex}$ is also sensitive to gas absorption. Regular baseline measurements correct the measured extinction for gas absorption. It should be noted that rapid changes in gas concentrations (e.g. NO_2) also require more frequent baseline measurements.

The calibration of the overall setup is performed by the following two steps:

1) Two point calibration of the nephelometer with Rayleigh scattering gases, typically CO_2 and particle free air.

2) Cross calibration of CAPS$_{pmex}$ and Nephelometer using non-absorbing particles. This is usually done by generating ammonium sulphate in a nebuliser. The light path length factor of CAPS$_{pmex}$ is determined by a cross calibration between the corrected light scattering coefficient measured with the nephelometer and the measured extinction coefficient with the CAPS$_{pmex}$.

An error analysis was carried out which took into account all sources of errors during calibration and during regular measurements. Sources of errors are:

- Nephelometer noise
- Nephelometer truncation error
- Error of calibration constants of the nephelometer
- CAPS$_{pmex}$ noise
- CAPS$_{pmex}$ calibration error (effective light path length)
- CAPS$_{pmex}$ baseline drift

The calculation of the particle absorption coefficient via the difference of extinction and scattering is possible with simple means. However, the description error propagation is more complicated due to the non-independent calibrations of the instruments. The full data processing chain and error propagation scheme is shown in Figure III-1.
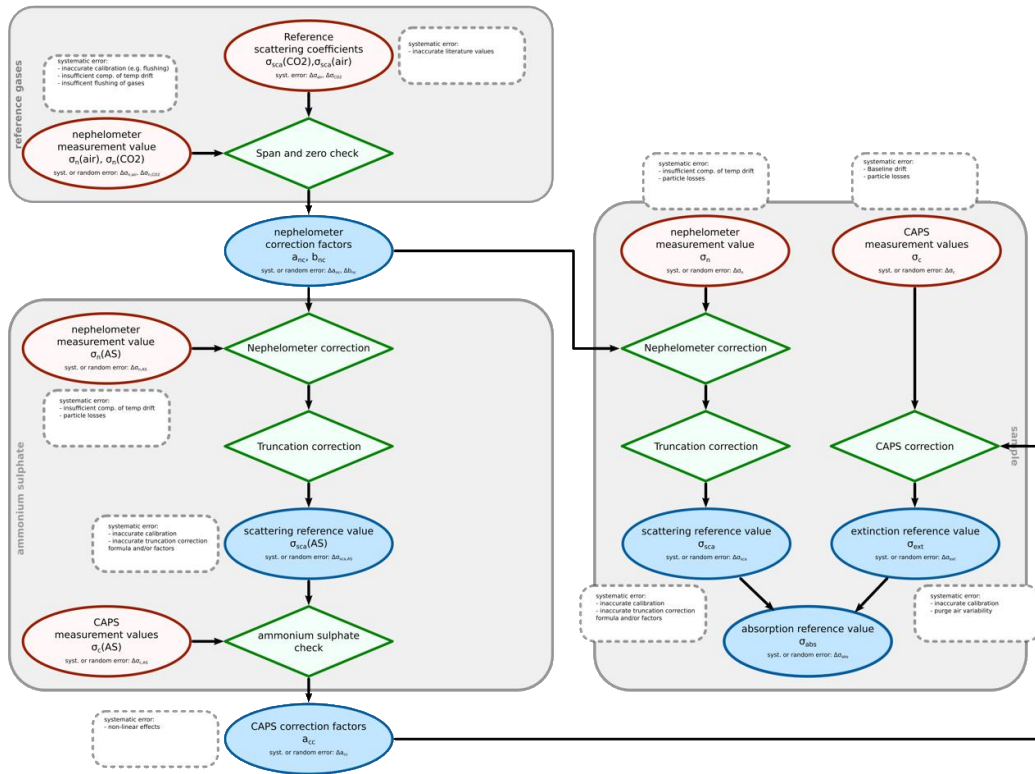
Figure III-1: Calibration chain and error propagation of a setup for measuring the particle absorption coefficient by the difference of particle extinction and scattering coefficients.

Instrumental noise

The noise characteristics of the nephelometer and the CAPS$_{pmex}$ were determined by a ten-day measurement with particle-free air. The noise, defined as the single standard deviation in an averaging interval, is plotted as a function of the length of the averaging interval (Figure III-2). It is noticeable that the noise of the CAPS$_{pmex}$ is much lower than the noise of the nephelometers especially for short averaging intervals. As the length of the averaging interval increases, the noise levels of the Aurora4000 and CAPS$_{pmex}$ become equal. It is suspected that a non-gaussian source of error (e.g. baseline drift) is causing the weaker decrease of noise in the CAPS$_{pmex}$.
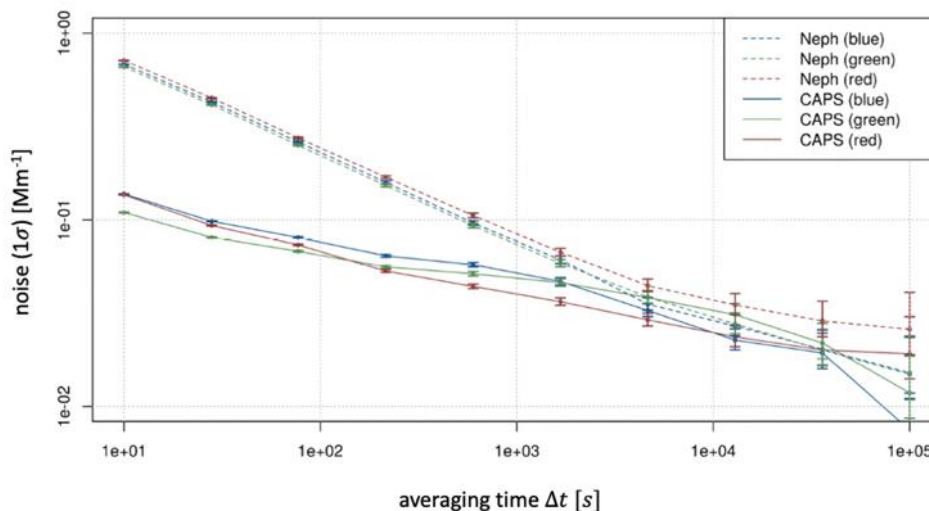

Figure III-2: Noise as function of the averaging time for Nephelometer (Aurora4000) and three CAPS$_{pmex}$ instruments.

Long term stability of the path length calibration factor of CAPS$_{pmex}$

The repeatability of the calibrations of the entire set-up is of essential importance. For this purpose, 18 full calibrations were carried out for a period of about one month. The resulting light path length correction factors are shown in Figure III-3. These factors also include the uncertainties of the nephelometer calibrations due to the cross calibration, which are between 2 and 3 %. Two instruments (630 nm and 532 nm) agree well, while the third instruments (450 nm) is about 5 % higher. However, this graph reflects the repeatability of the overall EMS calibration, which is about ± 2 %.

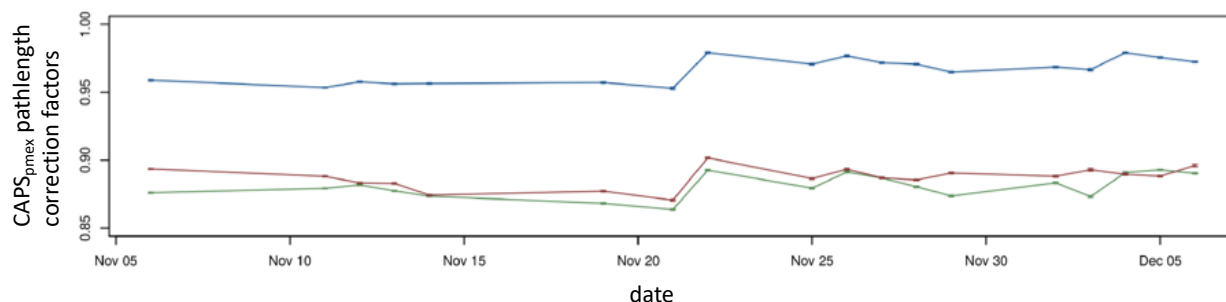Figure III-3: Series of repeated calibrations of the light pathlength factor of three CAPS$_{pmex}$.

For these measurements, the setup was changed as little as possible over the entire period and not moved. Transporting the setup would require a recalibration, as nephelometers in particular are sensitive to transportation if not handled carefully.

Independence of calibration constant

In the following, the interdependencies of the calibration constants are discussed. The nephelometer provides two calibration constants for each wavelength, one for the CO_2 calibration (slope of two point calibration) and the other for the baseline. The CAPS$_{pmex}$ also has two calibration constants, the effective light path length and the baseline. Since the baseline of the CAPS$_{pmex}$ is adjusted several times within a full calibration, it is not included here as a calibration parameter.

The correlation between the remaining three calibration constants for three wavelengths each is shown in a correlation matrix (Figure III-4). It is noticeable that the three baseline constants of the nephelometer correlate with each other. This may mean that either contamination of the cell has occurred or that there is an influencing factor in the electronics or opto-electronic components that affects all wavelengths equally. The CO_2 calibration factors on the other hand are less correlated. Another block with negative correlations can be seen between the nephelometer baseline and the CAPS$_{pmex}$ path length factor. This negative correlation allows the conclusion that the current baseline values of the nephelometer calibration influence the overall system to a large part. It could not be worked out whether technical improvements or an optimized measurement strategy for performing the calibration would lead to an improvement.
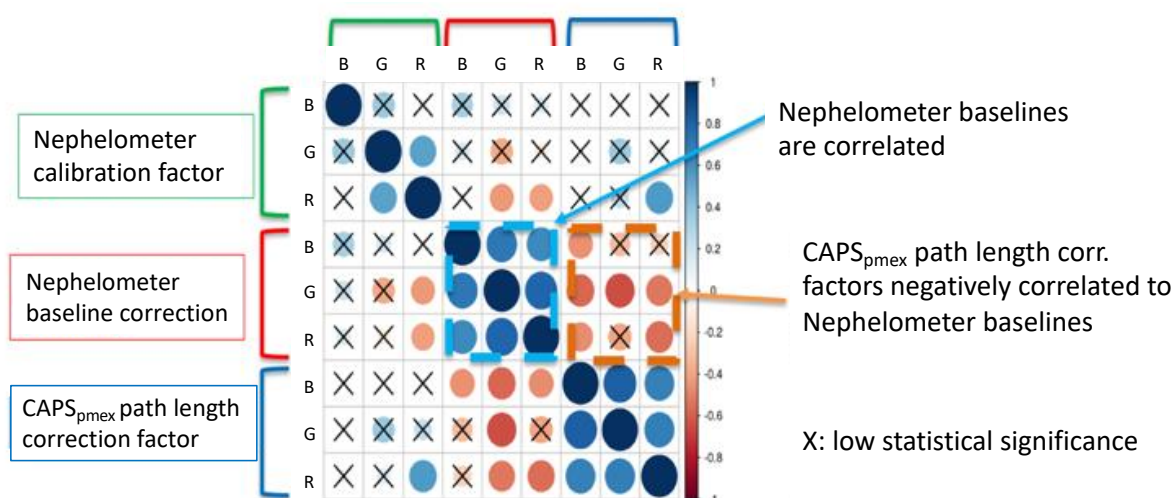

Figure III-4: Correlation matrix of calibration constants; B, G and R denote wavelengths 450nm, 530nm and 630nm.

Error of absorption coefficients

The error calculation was performed according to the scheme shown in Figure III-1 and the respective determined uncertainties were applied. The error varies depending on the single scattering albedo or the concentration of the aerosol under investigation. Therefore, in Figure III-5, the relative error is color coded as a function of single scattering albedo and extinction coefficient.

The errors can be very high for low extinction coefficients and high single scattering albedos. In order that the error does not exceed 10 %, the extinction coefficient must not be less than 10 Mm^{-1} and the single scattering albedo must not be larger than 0.95. It is easy to see that for an error of 4 % extinction coefficients of about 100 Mm^{-1} at low single scattering albedo (<0.2) are needed. In the field, with expected single scattering albedos between 0.7 and 0.9, extinction coefficients of about 100 Mm^{-1} would be required to have the error below 20 %.
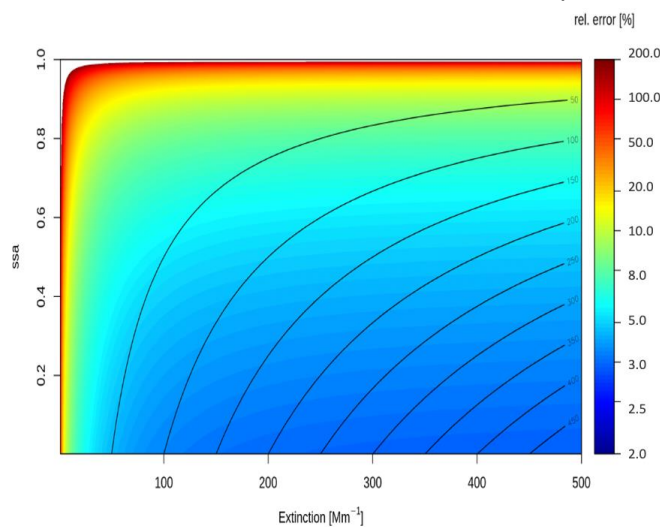

Figure III-5: Calculated relative error of absorption at 450 nm as function of extinction coefficient and single scattering albedo for an averaging time of.

The absolute error is composed of the noise of the scattering and extinction measurement, and the error of the baseline measurement. The values differ for the three wavelengths and amount 1.29 Mm^{-1} (450 nm), 0.98 Mm^{-1} (525 nm) and 1.14 Mm^{-1} (635 nm) for an averaging time of two minutes. Longer averaging times cannot significantly reduce the uncertainty, as the baseline drift is the dominating factor. Therefore, these values can be regarded as representative.

SI-traceability

The nephelometer is first calibrated with gases of known Rayleigh scattering coefficients. These are also called High and Low Span gases. Low span gas is usually air (particle free). This gas can be from filtered ambient air or from a gas cylinder. This gas is also used for recurring baseline measurements, so filtered air has become the standard. The high span gas is a gas of higher density and therefore higher Rayleigh scattering coefficient. CO_2 has become the standard against other possible gases, because the difference to the low span gas is high enough to perform a two point calibration with low uncertainty and because it is easy to handle and also available in sufficient purity. The measurement of the optical properties, the Rayleigh scattering coefficients, is carried out with an optical system whose geometry can be reproduced with simple means to ensure correct operation. The main source of error, the truncation error and the deviation of the light source from the Lambertian light source can be determined experimentally. The correction for truncation can be calculated exactly for known materials (e.g. those used during calibration). Corrections for atmospheric aerosols with partly unknown properties can be corrected with an estimable accuracy.

The $CAPS_{pmex}$ must be calibrated to determine the effective light path length. This is done with known non-absorbing aerosols. For this purpose, particles with a known low imaginary part of the refractive index can be used, so that the value of the light scattering is sufficiently close to the value of the light extinction. Ammonium sulfate or PSL particles are most commonly used.

Care must be taken that the aerosol transport losses to the $CAPS_{pmex}$ and nephelometer measuring cells are equal to avoid a bias of the calibration. Therefore, it is practical to use sub-micrometer particles. The light extinction coefficient is calibration free, so that only the actual dilution factor or the effective path length is determined. However, it has been shown that at high light extinctions (>1000 Mm^{-1}) a non-linearity can occur. If the non-linear range is not reached, the instrument can be used without any restriction.

Extinction minus scattering: Single device (CAPS$_{pmssa}$)

A key advantage of the CAPS$_{pmssa}$, manufactured by Aerodyne Research Inc. (USA) is that both extinction and scattering measurements probe the identical aerosol due to the common detection volume. A challenge is truncation of scattered light due to the openings in the sphere and light reflections at the glass tube guiding the aerosol, which results in a reduction of light collection efficiency. As part of the project it was confirmed the truncation enhancement by reflections [2]. Observed truncation agrees within uncertainty with theoretically expected curves, where the remaining uncertainty is dominated by unknown laser path length outside the integrating sphere from which light can be scattered into the sphere. The uncertainty associated with truncation correction is estimated to be ~4 % and 9 % for fine and coarse mode dominated aerosol, respectively. Therefore, it is recommended to restrict CAPS$_{pmssa}$ based absorption coefficient measurements to submicron-sized aerosol, i.e. to remove coarse particles using an impactor.

The CAPS$_{pmssa}$ is not fully traceable on its own as the effective path length relevant to the extinction measurement can vary between instruments and drift over time. Furthermore, a non-linearity was observed at high total loss (>1000 Mm^{-1}), whereas the degree of non-linearity varies between instruments. Therefore, the extinction channel needs to be referenced against a calibrated nephelometer using parallel measurements of a suitable non-absorbing aerosol. This makes it possible to determine the effective path length with 1 % uncertainty (Pfeifer et al. 2020). The scattering channel of CAPS$_{pmssa}$ is cross-calibrated against the extinction channel using sufficiently small aerosol particles with known phase function of Rayleigh scatters to minimize uncertainties. The scattering cross calibration factor can be determined with a precision of around 2 % [2].

The uncertainties in the measurements of the extinction and scattering coefficients were extensively studied. Both precision and drift (stability based uncertainty) were considered for more details) [2].

As pointed out in the literature, the purge flows that protect the high reflectivity mirrors shorten the effective optical path length of the cavity and slightly dilute the instrument sample flow. Therefore, a correction factor must be applied to in order to account for these changes. The correction factor was shown to vary less than 3 % over a period of about one year for CAPS$_{pmex}$[2]. However, this result was obtained under optimal laboratory conditions and may not be applied to equipment in the field, especially after transport. The CAPS$_{pmssa}$ is therefore not a stand-alone SI traceable system. It can be used as a secondary reference by cross calibrating with a nephelometer. The need and frequency to perform cross calibrations will then depend on the application.

Photothermal interferometry (PTI)

Method description

The measurement principle of the new photothermal interferometry (PTI) that has been developed within this project has been described in detail in a recent publication[5].

Photothermal interferometry measures the temperature increase caused by the absorption of light by a light absorbing substance. In the case of aerosol measurements, the temperature increase of the air is measured after light absorption by impurities in the air such as BC particles and NO$_2$ gas. By modulating the laser irradiation of the sample, a temperature modulation of the air occurs, the amplitude of which is directly proportional to light absorption coefficient of the aerosol. The temperature modulation causes a modulation of the local air density and thus a modulation of the refractive index of the air. This modulation of the refractive index can then be measured via interferometry.

Previous PTI designs have relied upon two lasers, one extremely stable laser for interferometry and another higher-powered laser, whose beam is amplitude modulated and absorbed by the light absorbing substances in the air. In the realization of PTI presented here (Figure III-6), the two lasers have been replaced by a single highly stable and high-powered laser (532 nm wavelength), which is amplitude modulated. This development is termed modulated single-beam interferometry (MSPTI).
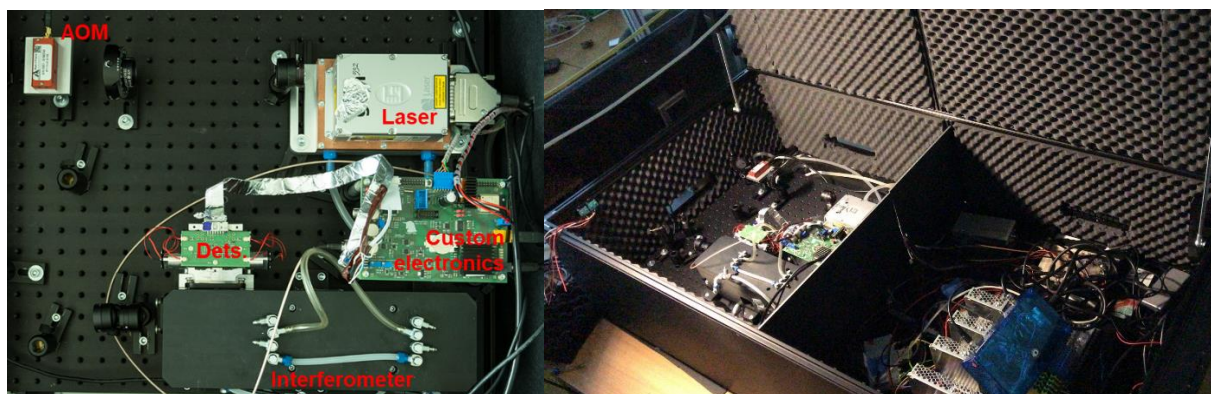
Figure III-6: The newly developed MSPTI. Left: top view of the sensor unit. Right: Whole MSPTI with sensor unit and power supply and data acquisition.

Compensation of trace gases

The instrument has been designed such that measurements of BC are free of artifacts caused by absorbing gases such as NO_2. A reference chamber is filled with the filtered ambient aerosol and any light absorption in this chamber is automatically subtracted from the total aerosol light absorption. To our knowledge, this is the first time that this has been achieved in an in-situ measurement of light absorption.

The current prototype instrument has been significantly improved from the version that is presented in our recent publication [5]. The interferometer is now constructed in a solid metal housing, the pressure chamber for controlling the quadrature point has been incorporated into the aerosol chamber and the quadrature point is controlled by a custom bellows. Furthermore, the commercial electronics units have been replaced by custom-built solutions.

Calibration

The MSPTI is calibrated using NO_2 gas. By switching from measurement mode to calibration mode the measurement chamber is filled with NO_2 gas and the reference chamber is filled with filtered lab air. The measured absorption is then compared to the literature absorption cross-section of NO_2 at the laser wavelength. This means that the MSPTI can be calibrated to a traceable primary reference and used to calibrated other light absorption-based instruments.

Detection limit and error analysis

The current detection limit (1σ) of the MSPTI is approximately 0.4 Mm^{-1} for NO_2 gas and an averaging time of 120 seconds (Figure III-7). It is up to a factor of two higher for BC particles due to statistical noise arising from very low numbers of particles in the detection volume at such low concentrations. This statistical noise is still subject to investigation.
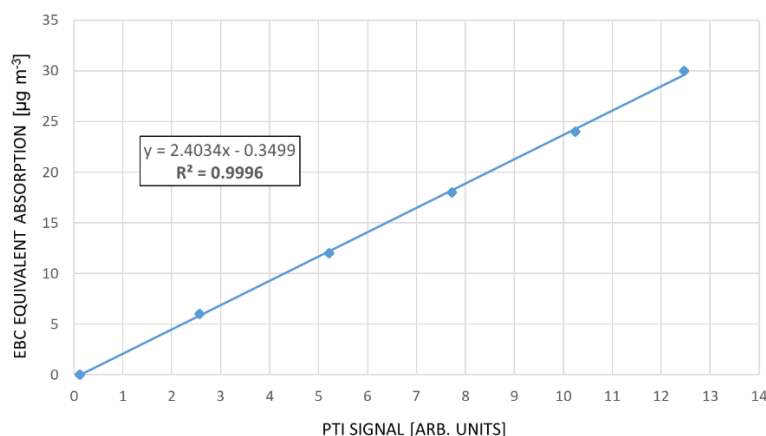

Figure III-7: Concentration series showing that the current detection limit is 0.4 Mm^{-1}. This corresponds to an eBC concentration of 40 ng m^{-3} (assuming a mass absorption coefficient of 10 m^2/g).

The main sources of error are related to the stability of the laser. Changes in lasing wavelength can be falsely interpreted as changes in absorption. The stability of the background measurement is also influenced by the laser stability and it is important to account for background drifts by measuring the background absorption every few minutes.

4.3.3 Summary of results

SI traceability and calibration

SI-traceable calibration is in all cases based on a calibration using gases, either the measurement of the light absorption in an absorption band (MSPTI) or the measurement of the Rayleigh light scattering coefficient in the $CAPS_{pmex}$-Aurora4000 setup. Therefore, only MSPTI and Extinction minus scattering based on $CAPS_{pmex}$-Aurora4000 are SI-traceable methods.

Both EMS methods ($CAPS_{pmex}$-Aurora4000 and $CAPS_{pmssa}$) perform a cross calibration using suitable non-absorbing aerosols. It is advantageous to have combined measuring cells ($CAPS_{pmssa}$) for measuring scattering and extinction to avoid bias due to particle losses. The PAX performs a calibration of the light absorption by an extinction measurement with a sufficiently low single scattering albedo.

SI-traceable method could be considered as primary standards as the calibration is reproduceable in any laboratory using certified gases. $CAPS_{pmssa}$ and PAX could instead be considered as secondary standards since these methods can be calibrated using primary methods. Furthermore, cross calibration between scattering and extinction (aerosol with high single scattering albedo) for $CAPS_{pmssa}$ and extinction and absorption (aerosol with low single scattering albedo) for PAX using aerosols can confirm the validity of the calibration, allowing these instruments to be used as a field reference.

Portability

For field applications it is important to discuss portability and subsequent actions to calibrate the setup or confirm calibration.

For $CAPS_{pmex}$-Aurora4000, a setup of multiple instruments has to be transported. Even if care is taken to rebuild the setup including the aerosol tube in its original configuration, recalibration is strongly recommended. For $CAPS_{pmssa}$ it could be confirmed by cross calibration that the calibration of the scattering and extinction channels have not changed against each other. MSPTI instruments require realignment of optics and recalibration, what limits the portability. For PAX, a calibration check after transport would be desirable. According to the user manual (Droplet Measurement Technologies, 2018), this could be done with a simple apparatus for measuring flame soot. Since the simple structure of the soot is not known a priori, this method can only be carried out with a larger degree of uncertainty.

Frequency of calibrations and baseline measurements

The frequency of calibrations was not investigated in details for all setup. For MSPTI, the long term long stability of the calibration could not be investigated due to time constraints. The baseline in MSPTI is measure continuously. For $CAPS_{pmex}$-Aurora4000, the stability of the calibration was found to be good for periods of a couple of months and the frequency of baseline measurements should be between 5 minutes and 15 minutes. For $CAPS_{pmssa}$ no specific measurements were done. It can be argued that the performance is similar to the $CAPS_{pmex}$-Aurora4000 setup.

Relative uncertainty and detection limit of absorption coefficients

For comparability of the accuracy of the derived absorption coefficients, the following scenarios were investigated:

- The instruments were equipped with a pre-impactor to avoid large truncation correction errors. For a focus of aerosols whose absorption coefficient is dominated by soot, this is not a significant limitation.
- Aerosols with extinction coefficients of 10 Mm^{-1} and 100 Mm^{-1} and single scattering albedos of 0.8 and smaller 0.2 were considered.
- Uncertainties were given for two minutes averages.

Relative uncertainties for EMS ($CAPS_{pmex}$-Aurora4000) were calculated using the error propagation scheme shown in section 4.3.2. The relative error for MSPTI cannot be given because the new design has just been developed and not enough independent calibration has been performed. No comparison with EMS ($CAPS_{pmex}$-Aurora4000) could be performed yet.

The detection limit of EMS ($CAPS_{pmex}$-Aurora4000) is dominated by the baseline drift of $CAPS_{pmex}$. The detection limits for two minutes averaging time 1.29 Mm^{-1} (450 nm), 0.98 Mm^{-1} (525 nm) and 1.14 Mm^{-1} (635 nm). The $CAPS_{pmssa}$ detection limit has not yet been determined. It can be argued that with similar noise of the

extinction and scatter measurements, the baseline drift also dominates the uncertainty. The value is therefore estimated to be about 1.0 Mm^{-1}.

The detection limit of MSPTI was determined to be 0.4 Mm^{-1} (1σ noise) for NO_2. Because of statistical noise due the low number of particles, the detection limit for particles is about a factor of two higher. In total, the 1σ detection limit is about 1.6 Mm^{-1}.

The detection limit for the absorption coefficient for PAX was calculated to be 0.33 Mm^{-1}. It should be noted, that this value is based on the instrumental noise and does not include uncertainties of baseline measurements. The expected relative error can not be estimated but was determined by intercomparison measurement a primary method, the $CAPS_{pmex}$-Aurora4000. The deviation of between the system was found to be about 10 %. With the available measurements, it cannot be estimated whether there are dependencies on the single scattering albedo or on the level of the absorption coefficient.

Multiwavelength measurements

The number of wavelengths in the EMS $CAPS_{pmex}$-Aurora4000 combination is realized through a three wavelength Nephelometer and three single wavelength $CAPS_{pmex}$. A covariance between few calibration constants of the nephelometer and $CAPS_{pmex}$ occurs. Therefore, the entire system cannot theoretically be considered a reference system with three fully independent wavelengths.

For $CAPS_{pmssa}$, it is in principle possible to combine several units of different wavelengths into a multi-wavelength setup. Although not carried out in this project, it can be concluded that a cross calibration or comparison with a multi-wavelength nephelometer should be carried out for all instruments at the same time so that changes in ambient conditions or test aerosols or gases do not cause a bias in the spectral response.

For nephelometers, $CAPS_{pmex}$ and $CAPS_{pmssa}$ no specific wavelengths are required for calibration and cross calibration with Rayleigh scattering gases and light scattering aerosols. However, both types of CAPS instruments require a measurement cell adopted to the wavelength because of the required high mirror reflectivity.

With MSPTI, a suitable combination of laser and calibration gas must be used for other wavelengths. An extension to a multi-wavelength setup therefore requires a high development effort and possibly also several calibration gases.

Since PAX is not calibrated with a gas like other photacoustic absorption photometers, but with aerosols, the technique can therefore be adapted to other wavelengths.

Cross sensitivity to absorbing gases:

Compensation of absorption by gases is done by baseline measurements with filtered air. As already mentioned, limitations of the compensation must be expected due to a time-delayed adsorption and release of the gases through the filter.

With $CAPS_{pmex}$-Aurora4000, $CAPS_{pmssa}$ and PAX, the regular measurements and zero measurements are carried out consecutively, so that a high temporal variability of the gases can cause further uncertainties. With the MSPTI, this is avoided by a simultaneous reference measurement.

Inlet and aerosol transportation losses:

To avoid transport losses, the aerosol lines should be kept as short as possible, and in the case of EMS ($CAPS_{pmex}$-Aurora4000) should be kept as equal as possible. However, since the focus is on soot particles in the submicrometer range, no significant losses are to be expected. To keep the influence of coarse mode particles in the truncation correction of the light scattering measurement of the two EMS methods small, a PM_1 impactor is recommended.

Conclusions

In summary (see Table III-1), two potential Si-traceable primary methods could be identified. These are the well-known extinction minus scattering method, based on a combination of nephelometer and extinction cell, and the not yet widely used PTI techniques. Due to limitations in portability, these setups are not well suited as field references in the current state of development. Two other set-ups are secondary standards, as direct calibration to SI units is lacking. However, these units are better suited as field references.

Table III-1: Summary of properties of the systems under investigation.

Method	Extinction minus Scattering		Photothermal Interferometry	Photoacoustic
Instruments	CAPS$_{pmex}$ -Aurora4000	CAPS$_{ssa}$	MSPTI	PAX
Wavelengths	450nm, 525 nm, 635 nm	630 nm, 780 nm	532 nm	870 nm
Detection limit (2σ noise, 2 minutes avg. time)	1.29 Mm^{-1} (450 nm) 0.98 Mm^{-1} (525 nm) 1.14 Mm^{-1} (635 nm)	Approx. 1 Mm^{-1}	Approx. 1.6 Mm^{-1}	0.33 Mm^{-1}
Relative error of absorption coefficient — ssa=0.2, b$_{ext}$=100 Mm^{-1}	5 %		Not specified	10 %
Relative error of absorption coefficient — ssa=0.2, b$_{ext}$=10 Mm^{-1}	9 %			10 %
Relative error of absorption coefficient — ssa=0.8, b$_{ext}$=100 Mm^{-1}	8 %	20 %		10 %
Relative error of absorption coefficient — ssa=0.8, b$_{ext}$=10 Mm^{-1}	41 %	30 %		10 %
Frequency of baseline measurements	Neph. baseline every 24h CAPS$_{pmex}$ baseline every 5 min	CAPS$_{pmssa}$ baseline every 5 min	Continuously	15 minutes
Long term stability of calibration	Several months	Not specified	Not specified	Not specified
Calibration method	Gas calibration of sca. and cross calibration between ext. and sca.	Cross calibration between ext. and sca.	Gas absorption	Calibration of scattering and absorption channels using particles
Si-traceability	Yes	No	Yes	No
Cross sensitivity to absorbing gases	Yes	Yes	No	yes
Portability	Yes with some efforts. Recalibration required.	Yes. Cross calibration recommended	Yes. Requires alignment of optics and recalibration	Yes
Requirements for full calibration	High and low span gas (e.g. CO2 and air) Scattering aerosol for cross calibration	Scattering aerosol for cross calibration	Calibration gas (NO$_2$)	Soot and non-absorbing particles with very high concentrations

All methods are subject to the high detection limit when compared with typical values of the absorption coefficient for ambient air. In addition, the EMS methods have higher uncertainties at high single scattering albedos. Therefore, field calibration of filter-based absorption photometers with ambient air is only possible in rare cases. However, with a transportable black carbon generator to produce black carbon particles with reproducible properties, field calibrations would be feasible and would also reduce the uncertainties due to gas absorption. It should be noted that such a black carbon generator would also support cross-calibration of PAX in the field.

In this compilation, no classical photoacoustic photometer has been considered, where the calibration is performed with absorbing gases. According to the criteria applied here, such a device would be considered as a primary standard [2, 4, 5]. The project successfully achieved the objective with these results. The work for the objective was led by TROPOS, with contributions fromconsortium members, PTB, NPL, IL, METAS, LNE, PSI, FHNW and NCSR Demokritos. .

4.4 Objective 4: A validated transfer standard for calibration of field absorption photometers
4.4.1 Introduction

The project evaluated most available black carbon measurement techniques with the aim of establishing reliable and traceable measurement methods. The field campaigns took place at two locations with different characteristics in terms of aerosol absorption levels, providing a real-world test for different absorption measurement techniques; one field campaign with calibrated instruments was organized at a location with high absorption levels (Athens, Greece, led by NCSRD) and one field campaign was performed at a clean background area in Pallas, Northern Finland, led by IL.

The standard reference material (SRM) were described as being similar to (1) freshly emitted combustion particles and (2) aged combustion particles respectively, and characterized as (1) size 50 - 100 nm, Single Scattering Albedo (SSA) 0.05 – 0.2 at 550 nm, and (2) size 200 - 400 nm, SSA 0.7 – 0.9 at 550 nm. Validation data for calibration with the "fresh" combustion aerosol source was acquired during a campaign in Athens.

4.4.2 Validation of calibration using "fresh" combustion aerosol sources

The Pallas campaign

The objective of the field campaign in Pallas was to estimate the sensitivity of different absorption techniques and test different absorption measurement methods in the field to better understand the challenges related to the demands of (low concentration) Arctic aerosol absorption measurements. Filter-based aerosol light absorption measurement methods are the most widely applied in the Arctic and these were the focus of this study. Aerosol light absorption was measured during a one-month field campaign in June–July 2019 at the Pallas Global Atmospheric Watch (GAW) station in northern Finland.

Throughout the campaign the aerosol was highly scattering with an average Single Scattering Albedo of 0.97. Aerosol concentrations were very low during the campaign, which imposed a challenge for the instruments' detection limits. The campaign was divided in two periods, based on the measured meteorological and aerosol characteristics: Period 1 (June 19 – July 7) and Period 2 (July 7 – July 17). The absorbing aerosol concentrations were very low, as is typical for the Polar Regions, although a notable increase in all measured aerosol extensive properties was seen in Period 2. Specifically, the aerosol number concentration increased on average by 25 % compared to Period 1, while the increase was the most pronounced in aerosol optical properties: extinction, scattering and absorption roughly doubled in Period 2 compared to Period 1. Overall, the average absorption (as determined by the MAAP) was 0.068 and 0.141 Mm^{-1} during the 1st and 2nd period, respectively.

The signal-to-noise analysis of the filter-based techniques suggested that the 1h-averaging of data provides a sufficient sensitivity at light absorption coefficients down to around 0.05 Mm^{-1} levels. In contrast to the filter-based techniques, the sensitivity of the indirect EMS method for measuring aerosol absorption was not adequate at such low concentration levels. An absorption coefficient on the order of >1 Mm^{-1} was estimated as the lowest limit, to reliably distinguish the signal from the noise.

In Table IV-1, the linear correlation coefficients and r^2-values between 1 hour average absorption values from the filter-based techniques (with the MAAP considered to be the reference) are summarized. In despite of the low signal levels (the whole campaign average absorption coefficient was about 0.1 Mm^{-1}), the filter-based instruments agreed within about 20 %.

Table IV-1: Linear correlation coefficient and r^2-values between 1-hr average absorption values from different filter-based techniques (MAAP considered to be the reference instrument)

Method	AE31*	AE33**	PSAP	COSMOS
MAAP ***	1.13x-0.01	0.70x+0.04	0.95x+0.02	0.66x+0.02
r^2	0.46	0.85	0.85	0.84

*The AE31 data measured was corrected for the multiple scattering of light by filter fibres by dividing the aerosol attenuation coefficient $\sigma_{0,\lambda}$ by a multiple scattering enhancement factor, $C_0 = 3.5$. The filter loading artifact was corrected using the Virkkula method, and the Pallas station specific correction factor k = 0.0038.

**The Pallas AE33 uses an internal multiple scattering correction factor $C_0 = 1.57$. This was corrected to a value $C_0 = 3.5$.

***MAAP measures absorption at a wavelength of 637 nm.

The Athens campaign

The „winter cammpaign" took place in Athens, Greece at the NCSR Demokritos site from 06/11/2019 to 09/01/2020. The aim was to assess the measurement uncertainties associated with different calibration materials (specifically fresh combustion-like), on representative field instruments commonly used in Europe, as well as to assess the stability and comparability of the systems running in parallel across a wide range of ambient aerosol black carbon levels.

All data were corrected following the best practice considered for each specific instrument before comparing the different techniques. The flow rate of each instrument was converted to standard (STP) conditions (0 °C, 1013 hPa), while zero checks were performed daily for all instruments. Specifically, the following corrections have been applied:

Athens laboratory experiment

The instruments were first tested during parallel sampling from a large 0.12 m³ laboratory mixing chamber. Black carbon aerosols of different properties were generated by means of three type of sources: (a) nebulizer (aquadag), (b) miniCAST and (c) two spark discharge generators (Palas, operated with argon, and Fasmatech, operated with nitrogen carrier gas). All instruments were sampling though the chamber, while the test aerosol entered the chamber along with an excess dry, particle-free air flow of 40 lpm. The experimental setup for BC production and analysis is shown in Figures IV-1. The RH and temperature in the chamber were monitored in order to confirm that they kept stable throughout the experiments. The number size distributions of the test aerosols in the size range between 10.2 nm and 461.4 nm (mobility diameter) were measured by means of a scanning mobility particle sizer (EC3080, CPC 3772, TSI). The aerosol flow rate was 1 lpm, whereas the sheath flow rate was 5 lpm. The number size distributions of larger particles (337 nm – 10 µm optical diameter) were measured with an optical particle size spectrometer (OPS 3030, TSI), operated at a flow rate of 1 lpm. The combined average size distributions for the different test aerosols are shown in Figure IV-2.
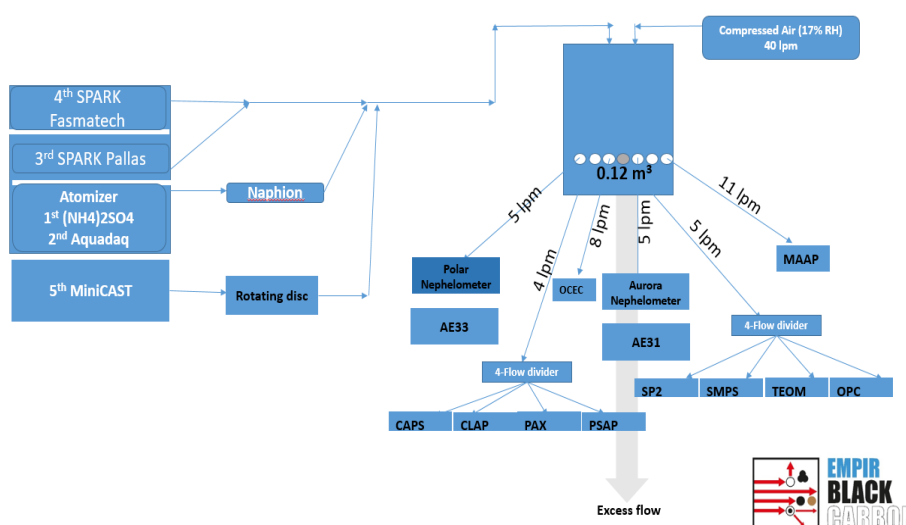

Figure IV-1: Schematic diagram of the experimental set up for instruments calibration
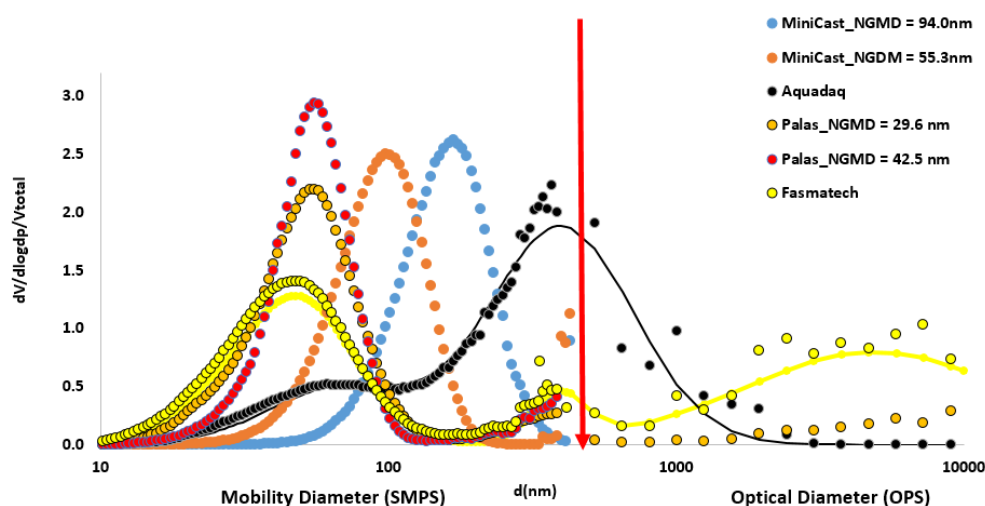

Figure IV-2: Volume size distribution for different types of test aerosol.

Figure IV-2 displays the mean size distribution measured by the SMPS and OPS systems. The mean size is calculated from all distributions obtained during stable conditions over a ~60 minute period for each type of experiment.

Throughout all the experiments, the single scattering albedo was below 0.40. The lower SSA values were seen in the aerosol produced by MiniCast ($SSA_{average, CAPS}$ = 0.19 – 0.20), while higher values were observed in the

aerosol produced by the SPARK discharge sources ($SSA_{average,CAPS}$ (Palas) = 0.33-0.37, $SSA_{average, CAPS}$ (Fasmatech) = 0.42), and Aquadaq ($SSA_{average, CAPS}$ = 0.47).

Figure IV-3 shows the comparison between different absorption measurement techniques for different types of test material. Overall, the instruments were very well correlated whatever the type of test aerosol, but the regression coefficients differ between different experiments, indicating that the instruments' response was affected by the specific characteristics of the test aerosol. The regression statistics for different absorption measurement techniques are summarized in Figure IV-3. Additionally, in Table IV-2 the regression coefficients (r^2) between Elemental Carbon and the eBC from the MAAP are summarized, while in Table IV-3 the ratios between eBC_AE33 and eBC_AE31 are presented for different types of test aerosols.
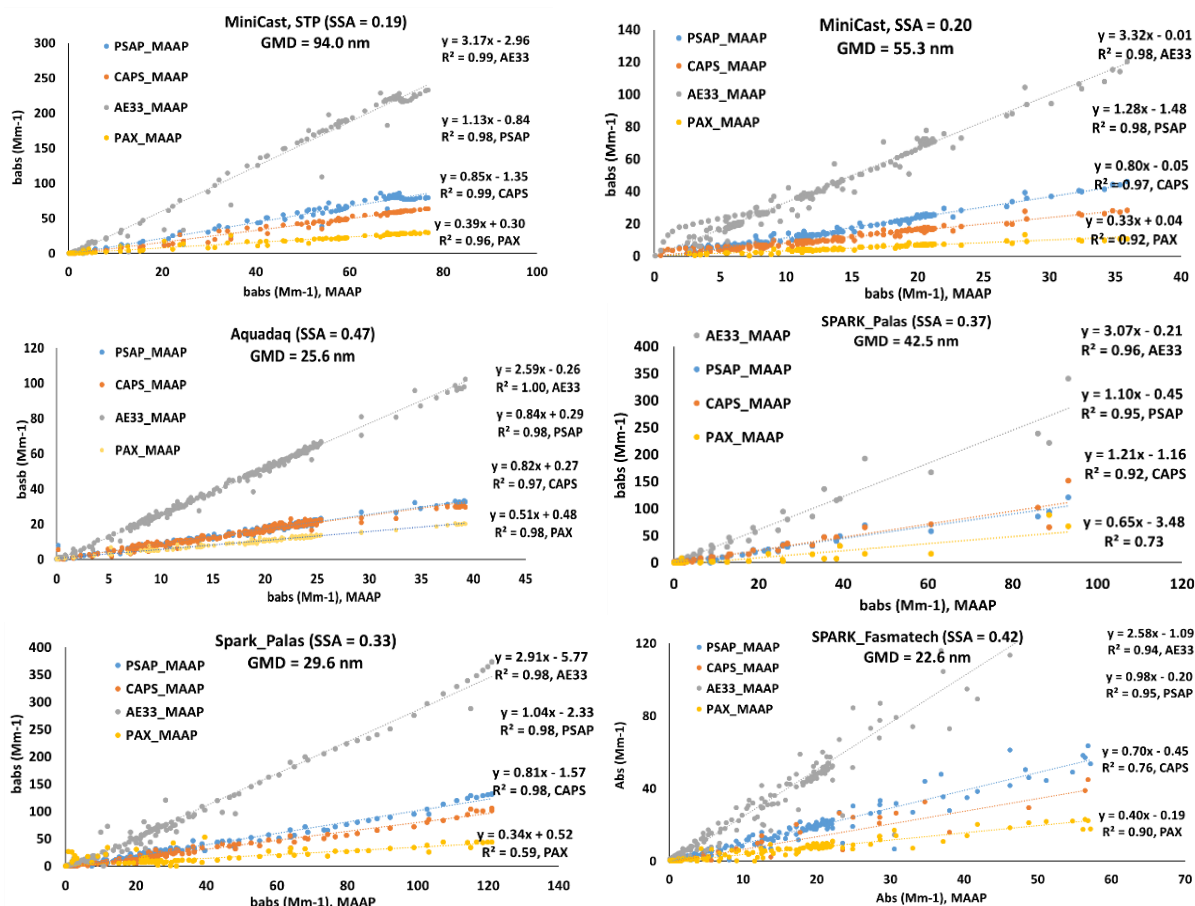

Figure IV-3: Correlation between different absorption measurement techniques. The MAAP is considered to be the reference instrument. GMD is the geometric mean diameter of the particle number size distribution. SSA is calculated from CAPS ($SSA = b_{scat}/b_{ext}$).

Table IV-2: Linear regression statistics between EC and eBC mass concentrations measured with MAAP.

	EC_eBC(MAAP)
MiniCast	0.73x+0.58 (R^2 = 0.98)
Aquadaq	0.54x+0.08 (R^2 = 0.99)
SPARK	1.08x+0.73 (R^2 = 0.88)

Table IV-3: Comparison between eBC measured with AE33 and AE31 for different types of test aerosol.

eBC	660nm	Type of aerosol
AE33/AE31 Slope	1.15	Room air
AE33/AE31 Slope	0.80	MiniCast (94.0 nm)
AE33/AE31 Slope	0.90	MiniCast (54 nm)
AE33/AE31 Slope	1.23	Aquadag

Athens Field campaign

After the end of the laboratory experiment, all instruments were placed at the GAW/ACTRIS NCSR Demokritos monitoring station, for a targeted field campaign from 06/12/2019 to 09/01/2020 in order to assess their comparative performance regarding the parameters under study (see Figure IV-4). The instrumentation was operated downstream of PM_{10} size selective inlets (except from OCEC, which was $PM_{2.5}$). The aerosol RH was nominally below 40 %, complying with GAW specifications, achieved through the use of Nafion dryers.

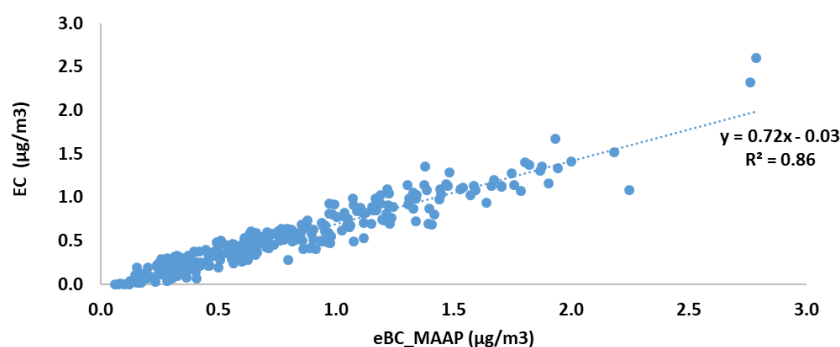Figure IV-4: GAW/ACTRIS NCSR Demokritos monitoring station and instrumentation

The 1 hour-average aerosol absorption coefficient during the campaign ranged between 0.3 and 26.3 Mm^{-1}. The average absorption for the whole period was 5.4 Mm^{-1}, whereas the average single scattering albedo was 0.83 (0.56 – 0.98) (Table IV-4). SSA was calculated as the ratio of the scattering coefficient, as measured by Nephelometer, to the extinction coefficient; the extinction coefficient was the sum of scattering coefficient and absorption coefficient as measured with MAAP.

Figure IV-5 shows the comparison between elemental carbon (EC) and eBC mass concentrations measured with the MAAP. A difference of about 30 % was observed between EC and eBC_MAAP (r^2 = 0.98). The average EC concentration was 0.59 μg/m³ while eBC_MAAP was 0.81 (μg/m³).

An overview of the results from the comparison between different absorption measurement techniques is given in Table IV-5, where the linear regression coefficients and r^2-values between different absorption measurement techniques (with the MAAP considered to be the reference absorption measurement technique) are listed. The comparison shows significant variability among different methods for different types of absorbing aerosol particles. This fact indicates that that the current corrections that are applied require further improvements.

Table IV-4: Average, minimum and maximum absorption coefficients and SSA values during Athens campaign

	b_{abs} (Mm^{-1})					SSA
	MAAP	**PSAP**	**CAPS***	**AE33**	**PAX**	
Average	5.4	5.2	4.3	13.0	2.2	0.83
Stdev	3.7	3.8	2.9	9.3	1.4	0.07
Min	0.3	0.3	0.1	0.9	0.2	0.56
Max	26.3	24.2	19.1	71.1	9.8	0.98

	EC (µg/m³)	eBC_MAAP (µg/m³)
Average	0.59	0.81
Stdev	0.39	0.49

Figure IV-5: Comparison between EC and eBC_MAAP.

Table IV-5: Linear regression coefficients and r^2-values between different absorption measurement techniques. The MAAP is considered to be the reference instrument. The slopes represent the total correction factor that can be used to harmonize different absorption measurements to the reference instrument (MAAP). VGMD is the volume geometric mean diameter of the average number size distribution; major size modes are marked in red.

	AE31	AE33	PSAP	CAPS	PAX
MiniCast, SSA=0.19 $VGMD_1$ = 163.2 nm		3.17x -2.96 r^2= 0.99	1.13x - 0.84 r^2 = 0.98	0.85x - 1.35 r^2 = 0.99	0.39x + 0.30 r^2 = 0.96
MiniCast, SSA=0.20 $VGMD_1$ = 97.0 nm	6.64x-2.39 r^2= 0.80	3.32x-0.01 r^2= 0.98	1.28x-1.48 r^2 = 0.98	0.80x - 0.05 r^2 = 0.97	0.33x + 0.04 r^2 = 0.95
Aquadaq, SSA=0.47 $VGMD_1$ = 69.4 nm $VGMD_2$ = 400 nm	3.93x-3.17 r^2 = 0.96	2.59 x-0.26 r^2=1.00	0.84x + 0.29 r^2 = 0.98	0.82x + 0.27 r^2 = 0.97	0.51x + 0.48 r^2 = 0.98
Spark Pallas (Argon), SSA=0.37 $VGMD_1$ = 26.1 nm $VGMD_2$ = 55.5 nm		3.07x - 0.21 r^2 = 0.96	1.10x - 0.45 r^2 = 0.95	1.21x – 1.16 r^2 = 0.92	0.65x – 3.48 r^2 = 0.73
Spark Pallas (Argon), SSA=0.33 $VGMD_1$ = 56.1 nm		2.91x – 5.77 r^2 = 0.98	1.04x – 2.33 r^2 = 0.98	0.81x - 1.57 r^2 = 0.98	0.34x + 0.52 r^2 = 0.59
Spark Fasmatech (N_2) SSA = 0.42 $VGMD_1$ = 22.8 nm $VGMD_2$= 48.9 nm $VGMD_3$= 393.5 nm $VGMD_4$ = 4.9 µm		2.58x – 1.09 r^2 = 0.94	0.98x - 0.20 r^2 = 0.95	0.70x – 0.45 r^2 = 0.76	0.40x - 0.19 r^2 = 0.90
Field (Athens)		2.41x + 0.07 r^2 = 0.97	0.98x - 0.08 r^2 = 0.94	0.76 x + 0.27 r^2 = 0.90	0.38x – 0.02 r^2 = 0.98
Field (Pallas)	1.13x-0.01* r^2 =0.46	0.70x +0.04** r^2 = 0.85	0.95x +0.02 r^2 = 0.94		

**The AE31 data measured was corrected for the multiple scattering of light by filter fibres by dividing the aerosol attenuation coefficient $\sigma_{0,\lambda}$ with a multiple scattering enhancement factor, C= 3.5.

**The AE33 uses an internal multiple scattering correction factor C_0 = 1.57. This was corrected to a value C = 3.5.

The overall agreement between absorption instruments is very encouraging in terms of their correlation and linear dependency against the same aerosol type. Especially the MAAP aethalometer and PSAP type of instruments are very well correlated and once a proportionality or calibration factor is applied they should provide measurements of aerosol absorption with high quality. For CAPS, we would recommend that further assessment of its behaviour is conducted, in particular with respect to sensitivity to the aerosol size range measured efficiently by the instrument. For PAX, the current experiments are in need of a baseline correction,

but confidence can be drawn from the excellent correlation achieved for most aerosol types and sources used here.

4.4.3 Outline calibration protocol

There are several distinct routes for calibrating commonly-used field black carbon instruments that involve collecting aerosol particles on a filter. They differ in the requirement for the aerosol calibration sources to be portable, and also reproducible and controllable in the field.

Field calibration using traceable aerosol sources

Field calibration based on traceable aerosol sources requires portable generators of "fresh" and "aged" calibration aerosol which are sufficiently reproducible in terms of both the relevant particle properties (especially particle size and SSA) and the aerosol particle concentration. Apart from the issue of portability, reproducibility of both properties and concentration has been demonstrated within this project to be a significant issue. For example, the output of the miniCAST 5201 BC needs to be considered in combination with the dilution system being used.

In practice, we do not consider it viable at this point to calibrate instruments in the field in this way, without several supporting field measurements such as size distribution (which could be done with SMPS/DMPS), mass concentration (which could be done with a TEOM instrument) and optical properties (which could be done with a multi-wavelength aethalometer or a $CAPS_{pmssa}$), to determine whether the sources are performing as required. The quantity of auxiliary equipment effectively makes such an approach unfeasible, even if the aerosol sources were portable.

Field calibration using aerosol sources and a calibrated reference instrument

As in Option I above, the emphasis in this route is to rely less on the traceability of the aerosol sources in isolation, and instead to rely on a secondary reference absorption instrument that has been traceably calibrated in a laboratory. The use of aerosol sources would be much preferable to relying on a comparison between the instruments using ambient aerosol, because a wider range of representative types and concentrations of aerosols could be used to challenge the instruments, within a period of a few hours.

This is likely to be an important route in future for sites where the removal of instruments from the site to a laboratory for calibration is undesirable. It is more feasible than the route described in Option I, as less equipment will need to be taken to the monitoring site, but the issue of portability of the aerosol sources remains. Also, it would be premature to designate the type of secondary reference instrument at this stage.

Laboratory calibration of instruments using traceable aerosol sources

The project has shown that this approach is both feasible and viable, although it has not been possible to establish all the necessary details and parameters. The basic outline protocol for this calibration route (Option II above) would take the form:

- "fresh" combustion aerosol (particle size 50 - 100 nm, SSA 0.05 – 0.2 at 550 nm);

  concentration (as optical absorption): 50 Mm-1;

  criterion for agreement with traceable reference: ± 10 %
- "aged" combustion aerosol (particle (size 200 - 400 nm, SSA 0.7 – 0.9 at 550 nm);

  concentration (as optical absorption): 50 Mm-1;

  criterion for agreement with traceable reference: ± 10 %.

If both these criteria were passed, if necessary after adjustment to the test instrument from its "as found" condition (but with no adjustment between the "fresh" and "aged" comparisons), the instrument would be considered calibrated. If an instrument could not be adjusted to meet both criteria, it could still be used to produce useful data, but these data could not be considered to be traceable.

Given the fast time response of most commonly-used field instruments, the averaging period of the comparison could be relatively short, for example one hour.

The protocol can easily be refined and extended, for example by specifying the particle size and SSA more narrowly, specifying other properties such as Angstrom Absorption Exponent (AAE), and specifying a level of agreement at several different concentrations, but the principle is the same.

The key practical elements that the calibration protocol will need to cover are:

1) The design and checks on the basic experimental set up, which allows parallel sampling of a common generated aerosol by the candidate instrument and the reference instrument. This will be similar to that for calibrating Condensation Particle Counters in ISO 27891.

2) The design, operational settings and performance criteria for the aerosol sources. As noted, these must include any dilution systems used, and must cover the reproducibility of the relevant particle properties, and the stability of the output concentration.

3) The design and calibration criteria of the reference absorption instrument. There are several different techniques available to provide verifiably traceable measurements of aerosol absorption, which need further experimental work before becoming fully validated methods for the purpose required here.

4) The design and calibration criteria for the auxiliary equipment required to monitor the calibration aerosol, in addition to the reference absorption instrument, to ensure that the basic protocol conditions are being met. As above, the particle size distribution could be determined with SMPS/DMPS. Depending on the measurement principle of the reference absorption instrument, the SSA could be determined separately with a CAPS$_{pmssa}$, for example. It may be advisable also to monitor mass concentration, which could be done with a TEOM instrument, and other optical properties, which could be done with a multi-wavelength aethalometer, for example, as part of a larger laboratory facility that would be impractical in the field.

4.4.4 Summary and Conclusions

The work for this objective was led by NCSRD, with contributions from consortium members, IL, NPL, TROPOS, PSI, FHNW and METAS. .

The project has provided a clear route for calibrating commonly-used black carbon instruments, and so has successfully achieved its objective.

In the short term, further development will involve laboratory calibration using sources of both "fresh" and "aged" combustion aerosol that are traceably-characterized in the laboratory at the time of calibration. Comparability and accuracy for aerosol particle light absorption measurement would be significantly improved. It would be premature to give definite figures for this, but there are indications that uncertainties will be reduced from around 30 % to around 10 % (at 95 % confidence).

Further validation of the laboratory calibration procedures is needed. In the medium term, as reproducibility of the aerosol sources is improved, it should be possible to carry out field calibrations of black carbon instruments, either with aerosol sources combined with a reference absorption instrument, or reference aerosol sources on their own.

5 Impact

Impact activities within the project included establishing a Stakeholder Committee; presentations to relevant standardisation and metrological committees, and scientific conferences, including the ETH Conference on combustion generated nanoparticles, the European Aerosol Conference and the International Aerosol Conference; training to 24 groups of people provided at TROPOS and at monitoring sites; and 5 papers published in peer-reviewed journals. One paper, *Radiative properties of coated black carbon aggregates: numerical simulations and radiative forcing estimates*, by Baseerat Romshoo et al, won the best poster award at the 2020 European Aerosol Conference.

The results achieved in the project were appropriately communicated to the stakeholders and end-user community of EC Directives and European standardisation activities such as CEN and BIPM (CIPM). Input and feedback was obtained from this community to improve the project impact and its outcomes.

During the course of the project the consortium ran a regular series of intercomparison and training workshops covering absorption photometers (for black carbon measurements) and integrating nephelometers (for scattering measurements).

Several of the partners were directly involved with the operation of black carbon monitoring sites for scientific and national network purposes, so that the results of the project were being implemented directly, for example through the establishment of improved calibration facilities and procedures.

In the short term, further impact will follow from laboratory calibration using reference sources of both "fresh" and "aged" combustion aerosol that are traceably-characterized in the laboratory at the time of calibration.

Comparability and accuracy for aerosol particle light absorption measurement will be significantly improved. It would be premature to give definite figures for this, but there are indications that uncertainties will be reduced from around 30 % to around 10 % (at 95 % confidence).

In the medium term, as reproducibility of the aerosol sources is improved, and further validation of the laboratory calibration procedures is carried out, it should be possible to perform field calibrations of black carbon instruments, either with aerosol sources combined with a reference absorption instrument, or reference aerosol sources on their own.

Impact on industrial and other user communities

In commercial terms the project will give a direct advantage to European black carbon instrument manufacturers, who will have early access to traceable calibration facilities for their current instruments, and who will also make use of the facilities to develop innovative designs much more quickly than would otherwise be the case. It will also offer a great advantage to European manufacturers of aerosol generators of the type that have been selected within the project as suitable to be calibration sources. End users would include government, environmental and citizen monitoring groups, who all employ black carbon measurement devices.

Impact on the metrology and scientific communities

The simplest direct impact of the research will be that measurements of black carbon become more accurate and more comparable in the aerosol monitoring networks across Europe, through the development of reference calibration sources for black carbon, primary national facilities and traceable calibration mechanisms.

Impact on relevant standards

The project outputs are expected to provide the basis for new documentary standards for monitoring black carbon by European and International standards-developing organisations like CEN and ISO. No such standards currently exist, and project partners regularly participated in the standardisation groups which are likely to develop them in future.

Longer-term economic, social and environmental impacts

In terms of socio-economic benefits, the project outputs will potentially lead to revised air quality legislation, based on black carbon, for which reliable measurement methods will be available.

Indirectly, the impact will be very widespread. In terms of scientific benefits, the improved measurements will be used directly within EU atmospheric aerosol projects, refining climate change models and mitigation proposals, and improving the quality of conclusions from cohort health studies looking at the effects of air pollution. Air quality measures to reduce black carbon emissions such as emission reduction and low emission zones have already been taken. However, traceable black carbon metrics to reliably quantify the success of these measures are not yet available. The results of the project will allow them to be addressed.

6   List of publications

1. Michaela N. Ess & Konstantina Vasilatou (2019) Characterization of a new miniCAST with diffusion flame and premixed flame options: Generation of particles with high EC content in the size range 30 nm to 200 nm, Aerosol Science and Technology, 53:1, 29-44, DOI:10.1080/02786826.2018.1536818 https://www.tandfonline.com/doi/full/10.1080/02786826.2018.1536818

2. Rob L. Modini, Joel C. Corbin, Benjamin T. Brem, Martin Irwin, Michele Bertò, Rosaria E. Pileci, Prodromos Fetfatzis, Kostas Eleftheriadis, Bas Henzing, Marcel M. Moerman, Fengshan Liu, Thomas Müller, and Martin Gysel-Beer, (2021) Detailed characterization of the CAPS single scattering albedo monitor (CAPS PMssa) as a field-deployable instrument for measuring aerosol light absorption with the extinction-minus-scattering method, Atmospheric Measurement Techniques https://doi.org/10.5194/amt-14-819-2021

3. Michaela N. Ess, Michele Bertò, Martin Irwin, Robin L. Modini, Martin Gysel-Beer &Konstantina Vasilatou, (2021) Optical and morphological properties of soot particles generated by the miniCAST 5201 BC generator, Aerosol Science and Technology https://doi.org/10.1080/02786826.2021.1901847

4. Sascha Pfeifer, Thomas Müller, Andrew Freedman, and Alfred Wiedensohler, (2020) The influence of the baseline drift on the extinction values of a CAPS Pmex, Atmospheric Measurement Techniques https://doi.org/10.5194/amt-13-2161-2020

5. Visser, B., J. Röhrbein, P. Steigmeier, L. Drinovec, G. Močnik, and E. Weingartner, (2020) A single-beam photothermal interferometer for in-situ measurements of aerosol light absorption, Atmospheric Measurement Techniques, https://doi.org/10.5194/amt-13-7097-2020

This list is also available here: https://www.euramet.org/repository/research-publications-repository-link/

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