22NRM02 STANBC

D2: Traceability chain

Report on the generation of a traceability chain for transferring light absorption calibrations between EMS and PTI reference methods and field instrumentation used for environmental measurements of BC using photoacoustic spectrometers as the transfer instrument

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Deliverable D1

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Glossary

AAE	Ångström absorption exponent
b_{abs}	Light absorption coefficient
BC	Black carbon
CAPS-PM_{ex}	Cavity attenuated phase shift-based extinction monitor
DMA	Differential mobility analyser
DOFR	Dekati oxidation flow reactor
EC	Elemental carbon
EMS	Extinction minus scattering
GMD_{mob}	Geometrical mean mobility-diameter
GSD_{mob}	Geometrical standard deviation (mobility-diameter based)
λ	Wavelength of light
N	Particle number concentration
NIR	Near infrared
OCU	Organic coating unit
OFR	Oxidation flow reactor
PALMA	Production of Ambient-Like Model Aerosols
PAM-ORF	Potential aerosol mass oxidation flow reactor
PAS	Photoacoustic spectroscopy
PAX	Photoacoustic extinctiometer
PTAAM	Photo-thermal aerosol absorption monitor
PTI	Photo-thermal interferometry
SOM	Secondary organic matter
SSA	Single scattering albedo
TC	Total carbon

TABLE OF CONTENTS

1. Summary

This deliverable outlines the development and implementation of a traceability chain for the calibration of light absorption measurement system for of black carbon (BC) aerosols. The approach enables reliable transfer of calibration from laboratory-based primary standards (e.g., Extinction Minus Scattering and Photo-Thermal Interferometry) to field-deployable instruments.

Within this framework, photoacoustic spectroscopy instruments are employed as transfer instruments. Their in situ operation and portable design make them ideal candidates to bridge primary reference methods and field monitoring instruments deployed in environments where the application of primary standards is impractical.

To establish this traceability chain, we evaluated a range of calibration materials, including combustion aerosols, commercial carbon black (Cab-O-Jet® 200), phenazine dyes (e.g., nigrosin), aged combustion aerosols, and ambient-like model aerosols. Each material was assessed based on optical properties, reproducibility, and suitability for calibration across different wavelengths. For wavelengths below 600 nm, we recommend the use of NO_2 as a calibration gas. For longer wavelengths, carbon black materials offer favourable characteristics such as spherical morphology and a constant Ångström Absorption Exponent (AAE). In particular, based on previous published data and our own measurements, the AAE of Cab-O-Jet® 200 remains constant in the range 450 nm ≤ λ ≤ 840 nm. The combination of constant AAE and spherical morphology simplifies optical modelling and wavelength extrapolation.

The deliverable also presents the laboratory calibration procedures for transfer instruments using Cab-O-Jet® 200. The protocol was validated in a controlled measurement campaign (Section 6) and is shown to enable reproducible calibrations with expected expanded uncertainties (k = 2) between 13.6% and 22.9%, for the PTI (operating at 808 nm) and the EMS (operating at 630 nm) respectively (Section 7). These uncertainty values apply to the case when the transfer instrument operates at the same wavelength than the primary standard. Additional uncertainties introduced by extrapolating absorption measurements from the operational wavelength of the primary standard to that of the transfer instrument are quantified and discussed in Section 8. The total calibration uncertainty, including the extrapolation process, was estimated to be 24.9% and 25.9% for the instruments used during the measurement campaign. Developing primary standard instruments that operate at the same wavelengths as transfer instruments would eliminate the need for spectral extrapolation, with the potential of a significant reduction of the calibration uncertainty.

2. Background

STANBC deliverable D1 introduced and described traceable calibration methodologies for two primary standard techniques for aerosol light absorption (Extinction Minus Scattering and Photo-Thermal Interferometry). These reference methods, based on first principles, allow the quantification of aerosol absorption coefficients with uncertainties below 10%, and can be calibrated directly using absorbing gases or well-characterized aerosols. However, their complexity and laboratory-bound nature limit their applicability in routine field deployments.

Photoacoustic spectroscopy offers an alternative approach with practical advantages: it provides direct in situ measurements of light absorption, is relatively easy to deploy, and can be adapted to operate at multiple wavelengths. Nevertheless, photoacoustic instruments are in the general sense not primary standards and require calibration against traceable references to ensure data quality and comparability.

This deliverable builds upon the foundations established in deliverable D1, presenting a strategy for traceable calibration of measurement systems based on photoacoustic spectroscopy, positioning them as suitable transfer instruments within a broader metrological framework. These instruments can act as an intermediary between laboratory-based primary standards and operational field instruments, facilitating the propagation of SI-traceable measurements outside of controlled laboratory environments (see figure 1).

The following sections describe the selection and evaluation of suitable calibration materials, the calibration procedures for photoacoustic instruments, and the uncertainty analysis of the traceability chain. This approach supports the overarching aim of the STANBC project: to establish a sound measurement framework for both aerosol light absorption coefficient and its conversion to eBC mass concentration, bringing traceability and consistency to both parameters, thereby improving comparability and accuracy across air quality monitoring networks in Europe (and worldwide) more accurate and comparable.

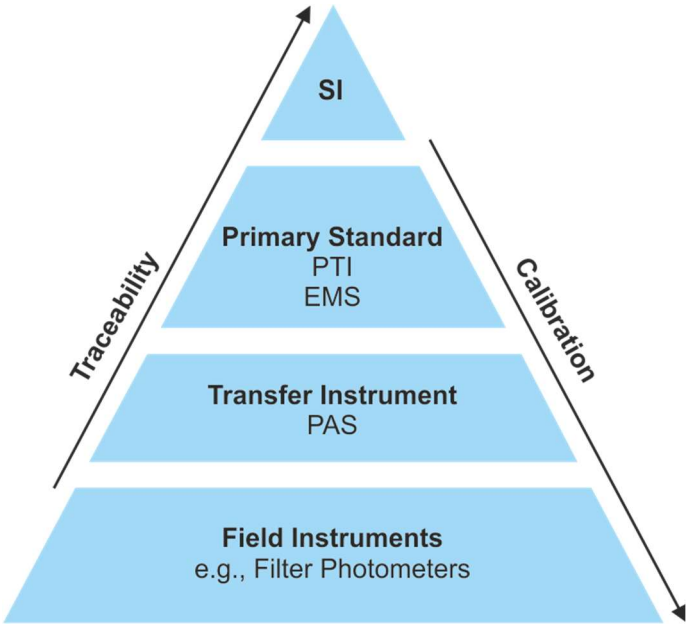

Figure 1. Conceptual traceability chain for aerosol light absorption measurements. Laboratory-based primary standards, Extinction Minus Scattering (EMS) and Photo-Thermal Interferometry (PTI), are used to calibrate instruments based on photoacoustic spectroscopy (PAS). PAS devices serve as transfer standards, enabling traceable calibration of field-deployable instruments outside of controlled laboratory environments.

3. Qualifications of primary standards

Primary standard instruments for aerosol light absorption measurements are based on fundamental physical principles. Their response is linear and reproducible, qualifying them as reference methods within a metrological framework. Nevertheless, their performance may be influenced by specific aerosol properties, which must be understood to ensure correct application in varying measurement contexts.

3.1. Extinction minus scattering

The principle of EMS is to determine aerosol light absorption by subtracting the measured light scattering from the total extinction. The experimental setup is detailed in the STANBC deliverable D1. Briefly, the system included one Aurora 4000 integrating nephelometer (Ecotech Pty LTD, Australia) and three CAPS PM_{ex} instruments (Aerodyne Research, Inc., USA). Integrating nephelometers measure the light scattering coefficient. The detector's design restricts the scattering angle range to 7° to 170°, and the light source does not conform to the ideal Lambertian light source as postulated in theory. The resulting truncation errors have been extensively studied (e.g., Anderson et al., 1996; Anderson and Ogren, 1998; Bond et al. 2009) and Mueller et al. (2011) proposed a correction method for the Aurora 3000 and the Aurora 4000.

The CAPS-PM_{ex} principle for measuring the light extinction coefficient is elucidated in Onasch et al. (2015). This method necessitates the precise effective light path length within the measuring cell. Furthermore, the CAPS-PM_{ex} baseline is susceptible to drift and requires frequent remeasurement to ensure accuracy. A numerical method for enhancing the quality of the baseline correction was published in Pfeifer et al. (2020).

It is possible to establish an SI-traceability of EMS as outlined in deliverable D1. The calculation of the particle absorption coefficient via the difference of extinction and scattering is possible with simple means. However, the description of error propagation is more complicated. Uncertainty increases notably when measuring aerosols with high single scattering albedo (SSA), due to the subtraction of two similarly large quantities. Deliverable D1 shows uncertainties exceeding the 10% target for SSA>0.8, which corresponds to highly scattering aerosols, and increases strongly at low concentrations (extinction coefficient below 20 Mm^{-1}).

3.2. Photo-thermal interferometry

Photothermal interferometry is an in situ method for measuring aerosol light absorption. A modulated pump light source heats the sample via light absorption, while a secondary interferometric laser detects the resulting changes in the optical path length of the sample air. The instrument's response is linear with respect to the aerosol absorption coefficient and exhibits negligible cross-sensitivity to scattering, making it suitable for high-SSA environments. Several interferometer and pump beam geometries have been applied (Moosmüller and Arnott, 1996; Sedlacek, 2006; Sedlacek and Lee, 2007; Lee and Moosmüller, 2020; Visser et al., 2020; Drinovec et al., 2022; Visser et al., 2023). Photothermal interferometry was used to measure absorption of coated soot in the Kalbermater et al. (2022) experiment. The method can be traceably calibrated to SI units based on first principles (Drinovec et al., 2022; Corbin et al., 2025) making PTI a suitable candidate for use as a primary standard for aerosol absorption measurements.

4. Transfer instruments

In the context of the STANBC project, photoacoustic instruments are used as an example of calibration transfer instruments within the traceability chain, facilitating the propagation of measurement accuracy from primary standards (EMS and PTI) to field instruments operating under diverse environmental conditions. The portability of these instruments make them particularly suited for use as an intermediary in the calibration chain, especially in environments where direct application of primary standards is impractical.

4.1. Specific characteristics of photoacoustic instruments

Photoacoustic spectroscopy is an in-situ technique used for measuring light absorption by gases or aerosols. It employs a modulated light source to heat the sample, resulting in pressure fluctuations that generate sound waves at the modulation frequency. For applications demanding very low detection limits, such as the quantification of aerosol absorption at ambient concentrations, photoacoustic instruments

typically utilize an acoustic resonator to amplify the sound signal, enhancing detectability by microphones or pressure transducers. This amplification occurs at specific resonance frequencies, typically in the kilohertz range, which are determined by the resonator geometry (Arnott et al., 2005). However, variations in gas temperature and composition can shift these resonance frequencies. To ensure consistent sensitivity and response, a tracking procedure is applied to continuously align the modulation frequency with the actual resonance. This can be implemented via a phase-locked loop, requiring a sufficient concentration of absorbing species, or through intermittent active excitation using a loudspeaker and frequency sweep. The latter approach may introduce additional uncertainty due to changes in the resonator's frequency response, which can depend on the location and geometry of the acoustic source.

Microphone cross-sensitivity to temperature and relative humidity can further affect the reproducibility of PAS measurements, depending on the specific components and configuration used (Raspet et al., 2003). These influences must be considered when deploying photoacoustic instruments as a transfer standard to ensure reliability and comparability of results across different systems and environments.

5. Evaluated calibration material

The accurate calibration of transfer instruments for aerosol light absorption requires well-characterized and reproducible calibration materials. In this section, we review a range of candidate materials with respect to their suitability for use in establishing traceable calibrations. Each material is assessed based on its physical and optical properties, stability, availability, and how closely it mimics real-world aerosol conditions. Particular attention is paid to parameters such as particle size distribution, morphology, volatility, and the spectral dependence of absorption. The materials considered include combustion aerosols, commercial carbon black, phenazine dyes, aged combustion aerosols, ambient-like model aerosols, and gaseous absorbers such as NO_2. The goal is to identify materials that allow for reliable and traceable transfer of calibration between primary standards and field-deployable instruments operating across a range of wavelengths.

5.1. Combustion aerosol

Combustion-based aerosol generators are widely used in BC studies due to their ability to produce particles with a broad range of sizes, morphologies, and chemical compositions, particularly in terms of the EC to TC ratio. By adjusting combustion parameters, such as the fuel-to-air ratio, users can generate aerosols that represent different sources.

Under fuel-rich conditions (where the fuel-to-air ratio exceeds the stoichiometric value), combustion tends to produce aerosols with a higher organic content and a lower EC-to-TC ratio. In contrast, fuel-lean conditions yield particles with a higher EC fraction, more representative of soot-like BC.

Several combustion systems are commonly employed for the controlled generation of such aerosols:

- **Diffusion Flame Generator**: A flame from a hydrocarbon fuel (e.g. propane or ethylene) is produced in a co-flow chamber, where the fuel is surrounded by an oxidizing air stream. The combustion is rapidly quenched with nitrogen to stop the oxidation process.
- **Premixed Flame Generator**: In this design, the fuel and oxidizer are mixed before ignition, leading to more efficient combustion and higher EC content. Quenching is typically done as in the diffusion flame setup.
- **Inverted Soot Generator**: This system features a downward-directed co-flow diffusion flame, where the buoyancy of the hot gases is opposed to the reactant flow. The configuration enables a stable flame and a stable aerosol output.
- **Spray Combustion Generator**: Mimicking jet engine combustion, this method uses a syringe pump to atomize fuel into a fine spray that combusts in an oxygen stream, initiated by a supporting flame.

Depending on the generator type and operating conditions, the size distribution of the produced BC particles can range from approximately 10 nm up to 300 nm in diameter. These particles consist of

aggregates formed from primary particles. Therefore, the lower size limit is set by the diameter of the primary particles.

Required equipment:

- Combustion aerosol generator (e.g. diffusion, premixed, or inverted flame type)
- Catalytic stripper or thermodenuder (optional, for removal of volatile organics and enhancement of EC fraction)
- Aerosol dilution system

Advantages:

- Enables stable and reproducible generation of combustion-derived aerosol.
- Particle properties (size, composition, EC-to-TC ratio) can be tuned by adjusting fuel and operational parameters.
- Useful for simulating real-world BC emissions under controlled laboratory conditions.

Disadvantages:

- High acquisition and operational costs associated with combustion systems.
- Non-spherical particle morphology complicates optical modeling, particularly for extrapolation to other wavelengths (e.g. via Mie theory).
- May require additional equipment (e.g. catalytic strippers, dilution systems) to control particle concentration and composition.

5.2. Carbon black

Carbon black is generic name for commercially available pigments composed of nearly spherical, submicron carbonaceous particles. These particles are produced by incomplete combustion or thermal decomposition of hydrocarbons and can be agglomerated to form larger aggregates. For metrological purposes, it is critical to use forms of carbon black that can be dispersed as individual, near-spherical particles, as aggregates present challenges for optical modelling using Mie theory. It is also important to note that carbon black is not the same material as “black carbon” (BC); the two may differ in their detailed properties (Long et al., 2013).

In this deliverable, we focus on a specific product (Cab-O-Jet® 200) which is representative of a class of aqueous carbon black dispersions developed for inkjet applications. Cab-O-Jet® 200 consists of surface-modified pigment particles that are stabilized in water by functional groups, allowing for the generation of monodisperse colloidal solutions. When aerosolized, these dispersions produce particles that closely resemble compacted soot spheres. Notably, the absorption Ångström exponent of these particles has been reported as AAE = 1.11 ± 0.03 for 500 nm ≤ λ ≤ 840 nm (Zangmeister et al., 2018), which is close to the theoretical value of AAE = 1 for ideal black carbon.

The aerosolized particle size depends on the dilution of the Cab-O-Jet® solution and the nebulization conditions. Typical values for the volume-equivalent mobility diameter range from approximately 95 nm to 160 nm. The spherical morphology and stable optical properties of Cab-O-Jet® particles make them particularly suitable for calibrating instruments across a range of wavelengths, especially in the near-infrared, where many in situ instruments operate.

Further information on the product is available via the manufacturer:
Cabot - Surface Modified Dispersions

Required equipment:

- Nebuliser (e.g., ATM 220 Topas GmbH, Germany)
- Dryer (e.g., Nafion dryer) to remove excess moisture

- Neutralizer (e.g., Kr85, soft x-ray) or conducting tubing downstream of the dryer to avoid electrostatic loses.
- Aerosol dilution system

Advantages:

- Commercially available and well-characterized material
- Reproducible generation of nearly spherical particles with AAE values close to unity

Disadvantages:

- Requires careful control of dilution and aerosolization to maintain particle monodispersity and size stability to prevent additional complexity in optical properties, particularly for extrapolation to other wavelengths
- Morphology and micro-structure is not identical to soot (black carbon)

5.3. Dyes

Phenazine dyes are commercially available organic compounds known for their broad absorption across the UV, visible, and NIR spectrum. Among these, the term nigrosin describes dyes that appears black due to their distinct optical properties.

When nebulized from aqueous solution, nigrosin forms spherical particles suitable for use in systems that require well-defined optical and morphological characteristics, like the calibration of absorption measurement devices (see, e.g., STANBC deliverable D1 and Foster et al., 2019). However, nigrosin's absorption spectrum is complex, particularly in the visible range, where absorption peaks are typically observed between 500 nm and 600 nm, resulting in a non-constant AAE.

As discussed in deliverable D1, this wavelength dependency must be thoroughly understood when calibrating a transfer instrument using a primary standard based on a different wavelength. Ensuring accurate calibration requires accounting for the spectral variation in absorption efficiency across the relevant range.

Required equipment:

- Nebuliser (e.g., ATM 220 Topas GmbH, Germany)
- Aerosol dilution system

Advantages:

- Readily available and water-soluble
- Forms spherical aerosol particles suitable for optical modeling
- Broad spectral absorption enables calibration over a wide wavelength range
- Previously validated as a calibration material for EMS and PTI systems (see deliverable D1)

Disadvantages:

- Relative to BC and carbon black, weak or negligible absorbers in the near infrared
- Complex wavelength dependence of absorption complicates AAE-based extrapolation
- Requires precise control of concentration and solution handling to ensure consistent aerosol properties

5.4. Aged combustion aerosols

Unlike freshly emitted black carbon, atmospheric carbonaceous particles undergo significant physical and chemical transformations through ageing processes. These transformations are driven by interactions with reactive gases such as ozone, hydroxyl radicals, and nitrogen oxides, resulting in the formation and condensation of SOM on existing aerosol particles. This coating alters not only the

chemical composition but also the morphology, optical properties (e.g. refractive index and SSA) of the particles.

The ageing process can lead to substantial modifications in the absorption characteristics of black carbon. Coated soot particles often exhibit enhanced light absorption due to intra-particle light scattering (so-called lensing effects) (Fierce et al., 2020) and shifts in size distribution. Consequently, calibration of light absorption instruments based on uncoated particles may not adequately represent real-world conditions, particularly in ambient monitoring scenarios.

In laboratory, aged combustion aerosols can be generated using environmental chambers, which simulate atmospheric chemistry under controlled conditions. However, these chambers are resource-intensive and time-consuming, making them less suitable for routine calibration. As a practical alternative, oxidation flow reactors can produce aged particles more efficiently (Ess et al., 2021). Devices such as the DOFR (Dekati Ltd., Finland) or the PAM-ORF (Aerodyne Research, USA) can be combined with combustion sources to generate reproducible aged aerosols with controlled degrees of SOM coating.

A more integrated approach is provided by the OCU (Keller et al., 2023), which combines an OFR and a dosing system for organic precursors. When paired with a controlled combustion source (e.g. miniCAST), this system enables the stable generation of aged aerosols that closely resemble those found in ambient air, as demonstrated in Kalbermatter et al. (2022).

Required equipment:

- Combustion aerosol source (e.g. miniCAST 6204 burner, Jing Ltd., Switzerland)
- Organic precursor dosing system
- Oxidation flow reactor (e.g. OCU, PAM-ORF, DOFR)
- Aerosol dilution system
- SOM precursor (e.g. α-pinene, toluene)

Advantages:

- Enables controlled production of aged aerosols representative of real atmospheric particles
- Allows systematic variation of SOM coating thickness and chemical composition
- Suitable for investigating instrument sensitivity to ageing-related artefacts

Disadvantages:

- Requires additional equipment beyond basic combustion sources
- Higher initial setup cost and operational complexity

5.5. Ambient-like aerosols

While aged combustion aerosols represent one pathway toward realistic calibration scenarios, true ambient particles are typically more complex, comprising a heterogeneous mix of primary and secondary aerosol species. To address this, ambient-like model aerosols are generated in laboratory settings using advanced facilities such as the PALMA system (Horender et al., 2021). This system is designed to simulate the compositional and morphological complexity of atmospheric aerosols under controlled and reproducible conditions.

The PALMA setup enables simultaneous generation and mixing of multiple aerosol types, including:

- Freshly generated soot particles
- Aged soot coated with SOM (e.g. from α-pinene ozonolysis)
- Inorganic salts (e.g. ammonium nitrate, ammonium sulfate)
- Mineral dust particles

Precise control of number and mass concentration is achieved using mass flow controllers, and aerosol mixing is performed in a custom-designed flow tube homogeniser. This 2.1-meter-long stainless steel tube allows the establishment of near plug flow conditions, ensuring homogeneity and residence time control. Environmental parameters such as temperature and relative humidity can also be manipulated to mimic various atmospheric conditions.

Required equipment:

- Stationary specialized complex facility like the PALMA system

Advantages:

- Enables stable and reproducible generation of complex aerosol mixtures under controlled laboratory conditions
- Composition, size distribution, and environmental conditions can be precisely tuned

Disadvantages:

- Requires significant laboratory infrastructure and expertise
- Complex mixing and ageing processes introduce operational challenges
- Many components (e.g. mineral dust and uncoated soot particles) are non-spherical, complicating optical modelling and wavelength extrapolation

5.6. Gaseous absorbers

Unlike the particle-based materials discussed above, gaseous absorbers such as NO_2, O_3 or O_2 offer a fundamentally different calibration approach based on known gas-phase optical properties. They can be used as traceable calibration standards for in situ absorption instruments, particularly those operating at shorter wavelengths ($\lambda < 600$ nm for NO_2 and O_3 and $\lambda \sim 760$ nm for O_2). The key advantage of using gaseous absorbers lies in their well-characterized absorption cross-section. Gaseous absorbers which are either chemically stable or stable under steady-state conditions then provide a stable reference signal. Gases may then enable the establishment of direct, SI-traceable calibration of instruments without the complexities introduced by aerosol particles, such as size distribution, morphology, composition, or mixing state.

Previous studies have demonstrated the successful use of NO_2 as a reference absorber in calibration procedures for PAS and PTI systems at 532 nm wavelength (Arnott et al., 2000; Nakayama et al., 2015; Drinovec et al., 2022). Ozone has also been demonstrated (Lack et al, 2006). The reference NO_2 concentration has been determined by the Beer-Lambert law within a PAS (Arnott et al., 2000) or using a reference-grade instrument (Drinovec et al., 2022).

Compared to ozone, NO_2 is often preferred due to its greater chemical stability and lower reactivity, which reduce the risk of secondary reactions or artefact formation during calibration. However, the use of NO_2 is limited to wavelengths $\lambda < 600$ nm, as its absorption decreases rapidly in the red and NIR spectral regions.

For instruments operating at longer wavelengths, calibration with the oxygen A-band at 760 nm has been demonstrated using tunable-laser PTI (Corbin et al., 2025). The reference concentration of O_2 can be determined using tunable-laser direct absorption spectroscopy (TLDAS), which provides simultaneous quantification of the calibration and background signals (Corbin et al., 2025).

It should be noted that the thermal relaxation timescales of gaseous absorbers can be different to that of particles. Therefore, in techniques where faster timescales are involved, such as typical PAS instruments operating at ~1 kHz, issues such as a cross-sensitivity to relative humidity can arise (Gillis et al., 2010). Karhu et al. (2022) have demonstrated a PAS operating at 90 Hz where this issue would be irrelevant. Timescales have been discussed in detail in Corbin et al. (2025).

Further information on the gas-phase calibration procedure using NO_2 can be found in STANBC deliverable D1.

Required equipment:

- For NO_2, a gas cylinder with traceably measured concentration or traceable NO_2 generator
- For O_3, an ozone generator
- For O_2, ambient air
- Temperature and pressure monitoring (gaseous absorption is a weak function of these quantities)

Advantages:

- Direct, SI-traceable calibration based on known gas-phase absorption cross-sections
- High reproducibility and low uncertainty
- Avoids complexities related to the aerosol particles

Disadvantages:

- Gases typically absorb at specific wavelength ranges (< 600 nm for NO_2 and O_3; ~760 nm for O_2), so cross-calibration to over wavelengths is required
- May not be representative of the absorption behaviour of aerosol particles in ambient conditions, depending on the design of instrument sample cells.

5.7. Comparison of calibration materials and recommendations

The selection of an appropriate calibration material depends on the intended application, the operating wavelength of the instrument, and the desired balance between traceability and representativeness of real BC aerosols, and practical constraints such as reproducibility and complexity.
Table 1 summarizes the advantages and disadvantages of the calibration materials evaluated in this section. Based on this comparative assessment, we recommend the following materials for routine calibration of aerosol absorption instruments within the STANBC traceability framework:

- **For wavelengths < 600 nm:**
  NO_2 is the preferred calibration standard due to its well-characterized absorption cross-section and high reproducibility. Its use enables calibration of transfer instruments without the artefacts associated with aerosol particles. However, its applicability is limited to shorter wavelengths due to its declining absorption in the red and NIR regions. Instruments that use wavelengths under 600 nm can, therefore, be considered primary standards. The appropriate calibration procedure is described within STANBC deliverable D1.
- **For wavelengths ≥ 600 nm:**
- Commercial carbon black dispersions, such as Cab-O-Jet® 200, offer a practical approach. These particles exhibit near-spherical morphology, a well-characterized AAE close to 1, and reproducible generation from colloidal dispersions. These properties make them well-suited for use in the calibration of transfer instruments and allow for relatively straightforward extrapolation across the NIR spectral range.
  Use the wavelength specific to the design of the instrument, in combination with a method for extrapolation to other wavelengths as appropriate.

While combustion aerosols and aged or ambient-like aerosols more closely replicate the complexity and variability of real ambient aerosol samples, they present greater challenges in terms of reproducibility, cost, and optical modelling. These materials are best suited for advanced validation exercises or artefact testing rather than routine calibrations.

Dyes, such as nigrosin, provide a broad spectral response and are valuable for calibration at specific wavelengths. However, their complex wavelength-dependent absorption behaviour and size distribution require careful characterization and are less suitable as a universal calibration material, particularly when extrapolation across wavelengths is required.

Table 1. Summary of evaluated calibration materials

Calibration Material	Advantages	Disadvantages
Combustion Aerosol	Realistic aerosol properties; tunable composition	High cost; non-spherical particles complicate modeling
Carbon Black (Cab-O-Jet® 200)	Commercially available; near-spherical particles; constant AAE ≈ 1	Setup complexity; risk of particle agglomeration
Dyes (Nigrosin)	Broad spectral absorption; used with primary standards	Complex wavelength dependence; wide particle size distribution
Aged Combustion Aerosol	Represents atmospheric ageing; reproducible coating	High equipment cost; added complexity
Ambient-like Aerosol	High realism; multi-component mixtures under controlled conditions	Requires extensive lab infrastructure; complex generation process
Gaseous absorbers (NO_2, O_3, O_2)	Can be quantified in situ; SI-traceable; highly reproducible; no particle artefacts	Limited to the absorption bands of the gas (NO_2 and O_3: $\lambda < 600$ nm; O_2 ~760 nm); some instruments may respond differently to particles and gases

6. Calibration of transfer instruments using Cab-O-Jet® 200

This section outlines the calibration of transfer instruments using a laboratory setup developed during the experimental measurement campaign at METAS in April 2024. The procedure aimed to establish a traceable link between the primary standards (EMS and PTI) and a field-deployable photoacoustic instrument, using Cab-O-Jet® 200 as the calibration aerosol.

6.1. Aerosol Production

The experimental configuration used to generate and deliver the calibration aerosol is illustrated in figure 2. The setup included:

- An ATM 220 nebuliser (Topas GmbH, Germany) to aerosolize the Cab-O-Jet® solution.
- A Nafion dryer (PERMA PURE MD-700-12S-1, UK) to remove excess moisture.
- An agglomeration tube to increase the GMDmob to 85–87 nm.
- A rotational disc diluter (MD19, Matter Engineering AG, Switzerland) to control particle concentration.
- Additional filtered air, regulated by a mass flow controller (MFC), to adjust total flow rate.
- A 12-port isokinetic flow splitter, designed to accommodate sampling flows between 0.15 and 10 $L \cdot min^{-1}$.

This setup enabled simultaneous sampling by multiple instruments under uniform and reproducible aerosol conditions.

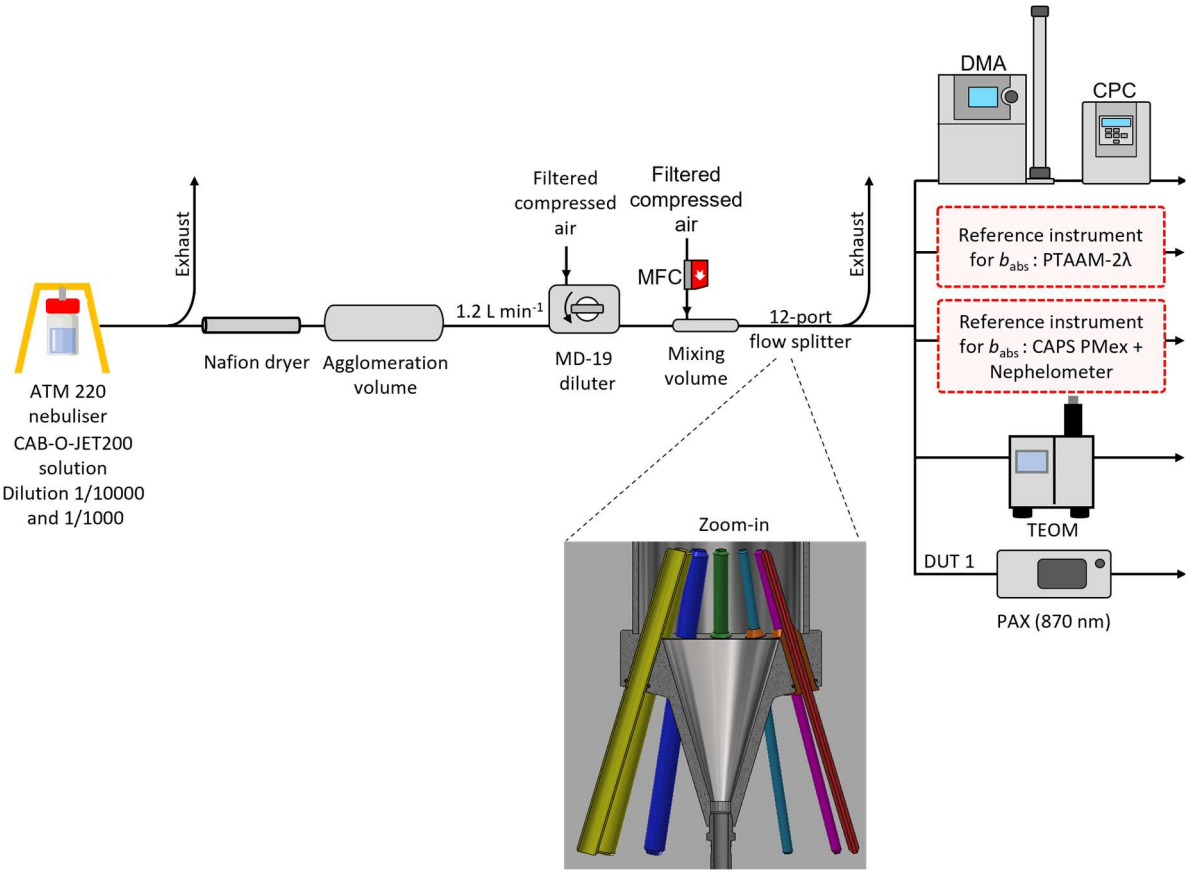

Figure 2. Schematic illustration of the experimental setup for the generation and measurement of Cab-O-Jet® 200 aerosol for the calibration of transfer instruments.

6.2. Measurement devices

Reference primary standards:

- **PTI reference:** PTAAM-2λ (Haze Instruments d.o.o., Slovenia), operating at 450 nm and 808 nm (Yus-Díez et al., 2025), previously calibrated using NO_2 and nigrosin aerosols (see Drinovec et al., 2022 and STANBC deliverable D1).
- **EMS reference:** A system comprising three CAPS-PM_{ex} monitors operating at 450 nm (one unit) and 630 nm (two units), combined with a polar integrating nephelometer (Aurora 4000, ACOEM, France) operating at 450 nm, 525 nm, and 630 nm. All instruments were either calibrated by the manufacturer or on-site following the calibration procedures documented in the respective manuals.

Transfer instrument to be calibrated:

- **Photoacoustic extinctiometer** (PAX-870-T, DMT, USA), operating at 870 nm.

Particle characterisation systems:

- **Scanning Mobility Particle Sizer** (SMPS): DMA 3082 + CPC 3752 (TSI Inc., USA), providing size distribution data such as GMD_{mob}, GSD_{mob}, and N.
- **Mass concentration**: Measured by a TEOM® 1405 (Thermo Scientific, USA), operated at 2.7 L·min^{-1} and 30 °C. This parameter is not required for the calibration procedure.

6.3. Calibration protocol

- Baseline measurements for PTI, EMS and PAX were performed for a duration of 1 hour before and after the calibration experiment, with data logged at 1 second resolution.
- The PTI instrument performed a zero measurement of 75 s after each measurement period of 45 s.
- Two calibration runs of at least 15 min were conducted using similar conditions:
  - Run 1: N = 6591 ± 61 cm^{-3}; GMD_{mob} = 87.0 nm ± 0.7 nm; GSD_{mob} = 1.92 ± 0.01
  - Run 2: N = 7231 ± 101 cm^{-3}; GMD_{mob} = 85.0 nm ± 1.1 nm; GSD_{mob} = 1.92 ± 0.01
- The light absorption coefficients (b_{abs}) were recorded:
  - PTI: Wavelengths 450 nm, 808 nm
  - EMS: 450 nm, 630 nm
  - PAX: 870 nm
- For calibration of the PAX, only b_{abs} values from PTAAM at 808 nm and PAX at 870 nm were considered:
  - Run 1: $b_{abs,PTAAM}$ = 27.4 ± 3.4 Mm^{-1} (808 nm); $b_{abs,PAX}$ = 35.8 Mm^{-1} (870 nm)
  - Run 2: $b_{abs,PTAAM}$ = 28.9 ± 3.6 Mm^{-1} (808 nm); $b_{abs,PAX}$ = 41.9 Mm^{-1} (870 nm)
- The AAEs, calculated from PTI data, were:
  - Run 1: AAE = 1.01 ± 0.11
  - Run 2: AAE = 1.06 ± 0.11
- Single Scattering Albedo:
  - Run 1: SSA_{PAX} = 0.15 ± 0.00 ; SSA_{EMS} = 0.27 ± 0.00
  - Run 2: SSA_{PAX} = 0.16 ± 0.00 ; SSA_{EMS} = 0.28 ± 0.00
- After normalization based on number concentration and conversion to the PTAAM wavelength of 808 nm using the AAE, the ratio of b_{abs} for the PAX and the PTAAM was calculated:
  - Run 1: $b_{abs,PAX}/b_{abs,PTAAM}$ = 1.41
  - Run 2: $b_{abs,PAX}/b_{abs,PTAAM}$ = 1.57

7. Uncertainty analysis and traceability chain

Table 2 summarizes the expected uncertainties in the determination of the absorption coefficient when calibrating a photoacoustic instrument against either a PTI or EMS reference instrument. The uncertainty associated with the estimation of the AAE, required if the absorption coefficient of the test instrument must be extrapolated to the wavelength of the reference instrument (see section 8), is not included in the presented uncertainty budget.

Table 2. Summary of the expected uncertainties in the determination of the absorption coefficient (b_{abs}) for the calibration of photoacoustic instruments (PAS), using either a photothermal interferometer (PTAAM; operated at 808 nm) or an extinction-minus-scattering setup (EMS; operated at 630 nm) as the reference instrument.

Source of uncertainty	**Relative standard uncertainty (k = 1)** PTAAM 808 nm (Monodisperse nigrosin calibration)	**Relative standard uncertainty (k = 1)** EMS 630 nm[a] (CO_2 calibration, high SSA, high concentration)
Reference instrument calibration	6.2%	11.1%
Mass flow measurement / Temperature and pressure PAS	2.0%	2.0%
Measurement PAS (Type A)	2.0%	2.0%
Expanded uncertainty PAS[b] (k = 1)	**6.8%**	**11.5%**
Expanded uncertainty PAS[b] (k = 2)	**13.6%**	**22.9%**
Additional uncertainties arising from wavelength extrapolation to 870 nm		
AAE estimation	10.4%[c]	5.5%[d]
Extrapolation to 870 nm	0.6%	2.6%
Expanded uncertainty PAS (k = 1)	**12.4%**	**13.0%**
Expanded uncertainty PAS (k = 2)	**24.9%**	**25.9%**

[a] The uncertainties are averaged uncertainties for EMS that apply only to concentrations with absorption coefficients between 25 and 50 Mm^{-1} and SSA < 0.5 at 630 nm, as observed in the experiments described in Section 6.2.

[b] Assuming the PAS measurement is done at the same wavelength as the reference instrument.

[c] See Yus-Díez *et al.* (2025)

[d] Refer to section 8.2 for details.

8. Extrapolation of wavelength from primary method

Primary standard methods such as EMS and PTI operate at fixed wavelengths, which may not always match the operational wavelength of the instrument under calibration. Consequently, wavelength extrapolation is often required to enable direct comparison of absorption coefficients between reference and test instruments. This process introduces additional uncertainty, which must be carefully quantified to maintain traceability.

8.1. EMS data processing and AAE estimation

The full data processing procedure for EMS measurements is detailed in STANBC deliverable D1. In brief, it includes the following key steps:

- Calibration of the nephelometer using CO_2.
- Calibration of the effective optical path length of the CAPS-PM_{ex} via cross-calibration with the nephelometer, using ammonium sulfate particles.
- Baseline corrections are applied to both instruments to account for instrumental drifts.
- Truncation correction is applied to the nephelometer data to compensate for angular limitations of the detector.

Once these corrections are made, the aerosol light absorption coefficient is obtained as the difference between the extinction (CAPS-PM_{ex}) and scattering (nephelometer) measurements

8.2. Uncertainty of the determination of the AAE

To extrapolate across wavelengths, the AAE is calculated. For a three-wavelength case, AAE is derived from the logarithmic ratio of absorption coefficients and wavelengths. In setups with three wavelengths, as in the EMS configuration used here, AAE is estimated via power-law fitting of b_{abs} as a function of wavelength.

During a series of experiments conducted at TROPOS, within the framework of STANBC, the average uncertainty (single standard error) of the AAE was 0.08 within the range of $1.34 \leq AAE \leq 1.57$ for the EMS operating at wavelengths 450 nm, 525 nm, and 630 nm. The relative uncertainty (single standard deviation) for a mean AAE of 1.46 amounts 5.5%.

8.3. Uncertainty of extrapolation

The uncertainty introduced by extrapolating EMS data from its upper wavelength limit (630 nm) to the operating wavelength of the PAX (870 nm) was assessed using error propagation techniques:

- Extrapolation-only uncertainty (double standard error):
  - Extrapolation from EMS to PAX (630 → 870 nm): 5.2%
  - Extrapolation from PTI to PAX (808 → 870 nm): 1.2%

9. Conclusions

This deliverable has reviewed and evaluated a range of calibration materials suitable for establishing traceability in the calibration of transfer instruments using primary reference standards. Our analysis supports a differentiated approach based on the operating wavelength of the transfer instrument.

For transfer instruments operating at wavelengths below 600 nm or those using light sources that coincide with gas-phase absorption features, such as the oxygen A-band, traceable calibration can be achieved directly. In such cases, these instruments may be treated as primary standards, provided they are calibrated following the procedures outlined in STANBC deliverable D1 using gaseous absorbers such as NO_2, O_3, or O_2.

For transfer instruments operating at wavelengths above 600 nm, we recommend the use of carbon black-based materials as calibration standards. In Section 6, we detail a calibration protocol using Cab-O-Jet® 200 as a model carbon black material. The expanded uncertainties (k = 2) associated with this procedure are estimated to lie between 13.6% and 22.9%, for the PTI (operating at 808 nm) and the EMS (operating at 630 nm) respectively. These uncertainties cover the case when the transfer instrument operates at the wavelength of the primary standard.

Section 8 presents the additional uncertainty related to the extrapolation of the absorption coefficient from the wavelength of the primary standard to the wavelength of the transfer instrument. Although the expanded uncertainty (k = 2) of extrapolation is irrelatively minor, 1.2% for the PTI (extrapolated from 808 nm to 870 nm) and 5.2% for the EMS (extrapolated from 630 nm to 870 nm), extrapolation also requires the determination of the AAE, which can have a large uncertainty. The resulting total expanded uncertainty (k = 2), taking extrapolation and AAE determination into account, was found to be 24.9% and 25.9% for the instruments used for the calibration campaign described in this document. Developing primary standard instruments that operate at the same wavelengths as transfer instruments would eliminate the need for spectral extrapolation, reducing the overall calibration uncertainty.

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