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Characterization and Demonstration of a Black Carbon Aerosol Mimic for Instrument Evaluation

Christopher D. Zangmeister¹, Courtney Grimes², Russell R. Dickerson³, and James G. Radney¹

1. Material Measurement Laboratory, National Institute of Standards and Technology, Gaithersburg, Maryland, USA
2. Department of Chemistry, University of Maryland, College Park, Maryland, USA
3. Department of Atmospheric and Oceanic Science, University of Maryland, College Park, Maryland, USA

CONTACT Christopher D. Zangmeister cdzang@nist.gov Material Measurement Laboratory, National Institute of Standards and Technology, 100 Bureau Drive, MS 8320, Gaithersburg, MD 20899, USA.

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Abstract

This study describes the characterization of a H₂O-dispersible, highly-absorbing carbonaceous nanomaterial that mimics the morphological and spectroscopic properties of aged black carbon aerosol (BC). When atomized from aqueous suspension, the material forms particles with a collapsed morphology resembling aged soot or BC. The material is > 90 percent elemental carbon and has a mass absorption coefficient (MAC) and spectral dependence consistent with BC values published in the literature. The MAC at a wavelength of 532 nm decreased monotonically from 8.5 to 5.8 m² g⁻¹ for aerosol with mobility diameters between 150 nm to 500 nm. The single scatter albedo (SSA) at wavelengths of 405 nm and 660 nm was a function of both wavelength and mobility diameter and increased from 0.1 to 0.4 with mobility diameters between 150 nm to 400 nm. The Ångström absorption exponent (AAE) between λ = 405 nm and 780 nm decreased monotonically from 1.4 to 0.6 for aerosol with mobility diameters between 150 nm to 400 nm. We demonstrate that this material can be used for fast, efficient calibration of aerosol photoacoustic spectrometers and for evaluation of spectroscopic-based measurements of aerosol mass concentration using in-situ photoacoustic spectroscopy (PAS) and filter-based light attenuation measurements for up to 50 µg m⁻³, enabling inter-method and inter-laboratory instrument comparison.
Introduction

Black carbon aerosol (BC) in the atmosphere impacts climate (IPCC) and endangers human health, yet the global BC budget remains uncertain by more than a factor of two (Andreae and Ramanathan 2013; Bond et al. 2013; IPCC 2013; Landrigan et al. 2018; Lelieveld et al. 2015). Quantitative, intercomparable aerosol measurements have been a focus of steering committees, workshops, and published reports (Baumgardner et al. 2012; NIST 2011). These groups have issued suggestions on developing nanomaterials and methods for instrument calibration, evaluation and intercomparison with the goal of enabling comparability and data harmonization in the reporting and agreement of measured values (Baumgardner et al. 2012). A workshop of more than fifty experts was convened in 2011 at the 10th International Conference of Carbonaceous Particles in the Atmosphere (IC-CPA) in Vienna, Austria and suggested the development of BC reference materials (RM) to be used for calibration of filter-based, in-situ incandescence and light absorption measurements (Baumgardner et al. 2012). Similar recommendations were issued at a workshop on Aerosol Metrology and Needs for Climate Science at the National Institute of Standards and Technology (NIST) in Gaithersburg, MD in 2011 (NIST 2011). These workshops set milestones for the demonstration and development of RMs for aerosol instrument inter-laboratory and inter-method comparability and calibration (Baumgardner et al. 2012; NIST 2011).

BC is defined as a class of solid, nearly elemental carbonaceous nanomaterials formed during the incomplete combustion of carbon-containing fuels, and composed of aggregated spherical monomers agglomerated into larger particles with a complex lacey (freshly emitted) or compacted (aged particles) morphology (Bond and Bergstrom 2006; Bond et al. 2013). Like most other elemental carbon materials (e.g. graphene, graphite, etc.), BC strongly absorbs light across the UV to near-IR spectral region (i.e. the solar transmission window), thereby impacting
the energy balance of the atmosphere (Bond and Bergstrom 2006; Bond et al. 2013; Lam et al. 2012; Zangmeister et al. 2018). The BC mass concentration ($M_{BC}$, g m$^{-3}$) is of particular interest, where it contributes to regulatory compliance for fine particulate matter (PM$_{2.5}$), and is involved in short-term transient concentrations and long-term records from measurements in soil, snow, and ice (Lim et al. 2014; Schmidt et al. 2001; Schwarz et al. 2012).

Two methods are often used to quantify $M_{BC}$ from the materials intrinsic optical properties: *in-situ* light absorption using photoacoustic spectroscopy (PAS) and *ex-situ* light attenuation using filter-based methods; here, *in-situ* denotes that the particles are suspended in air when the measurement is performed. Photoacoustic spectroscopy of absorbing materials (gas, aerosol, etc.) uses a transducer (microphone) to measure a pressure wave associated with the thermal relaxation of absorbed light (Havey et al. 2010). It is assumed that all absorbed energy is converted to heat and detected by the transducer. Other pathways of energy loss, such as evaporation of volatile species may impact the quantification of PAS measurements (Langridge et al. 2013; Radney and Zangmeister 2017). Aerosol mass concentration can be calculated from the measured photoacoustic response, via the aerosol absorption coefficient ($\alpha_{abs}$, m$^{-1}$), where $\alpha_{abs}$ is the product of the number density ($N$, m$^{-3}$) and the aerosol absorption cross-section at a given wavelength ($\lambda$), $C_{abs}(\lambda)$ (m$^2$), measured

$$\alpha_{abs}(\lambda) = N * C_{abs}(\lambda) = N * m_p * MAC(\lambda) = M * MAC(\lambda)$$

(1)

where $m_p$ (g) is the average particle mass, $MAC(\lambda)$ (m$^2$ g$^{-1}$) is the mass absorption coefficient for the measured distribution at a given $\lambda$, and $M$ (or $M_{BC}$, g m$^{-3}$) is the ensemble mass concentration (Radney and Zangmeister 2015; Radney and Zangmeister 2017; You et al. 2016). From Eq. 1, aerosol absorption measurements of $\alpha_{abs}(\lambda)$ enable $M$ to be calculated if the $MAC$ of the ensemble or particle is known.
Measurement of gas phase spectroscopic properties (e.g. $C_{\text{abs}}(\lambda)$) can be directly linked to the International System of Units (Système International, SI) using materials with calculated and experimentally verified spectral line intensities and absorption coefficients (see HITRAN, etc.) (Gordon et al. 2017). This enables instrument quantitative evaluation, calibration, and inter-comparability of instruments and methods. Conversely, there is no HITRAN analog for aerosolized nanomaterials, complicating the reporting of measurements derived from aerosol spectroscopic values, such as $M$. Aerosol spectroscopic properties ($C_{\text{abs}}(\lambda), \text{MAC}(\lambda)$) of highly absorbing materials, such as BC, are a function of the materials’ complex refractive index, the size of individual monomers, the arrangement of monomers (particle morphology), the particles size (e.g. mobility diameter), and the internal mixing state (Moosmüller et al. 2009; Zangmeister and Radney 2018). These parameters are a function of particle formation conditions such as the fuel used, the fuel to $\text{O}_2$ ratio, and the flame temperature (Colbeck et al. 1997; di Stasio and Braun 2006; Schnaiter et al. 2006; Zangmeister and Radney 2018; Zangmeister et al. 2018). Thus, BC $\text{MAC}$ cannot be described by a single value, but is a function of formation conditions, as well as particle size and morphology (Zangmeister and Radney 2018).

Filter-based detectors measure the change in light transmission through a filter as particles are deposited as a function of time. Filter attenuation is derived using the Beer-Lambert law ($I_0/I$), and is converted to $M_{\text{BC}}$ using an instrument-specific mass attenuation coefficient ($\text{MATC}$) at one or more $\lambda$. Because of the portability, robustness and ease of operation of filter-based measurements, they are widely deployed in field studies to determine $M_{\text{BC}}$ and wavelength dependent aerosol attenuation, but a number of factors can impact their accuracy. In principle, the $\text{MATC}$ is a function of the same parameters that influence aerosol spectroscopic properties (RI, monomer size, morphology, etc.), but must also include contributions from the scattering
cross-section of individual particles and other filter-dependent effects such as the physical characteristics of the filter medium, multiple scattering of light by the filter and particles, particle shadowing, volatile particle evaporation and gas condensation (Arnott et al. 2005; Laborde et al. 2012). Each of these parameters adds complexity and may limit the accuracy of filter-based measurements (Arnott et al. 2005). This method will be more thoroughly characterized in a follow-up paper.

Recent studies highlight the need for developing rigorous methods of quantification, comparison, and validation of $M_{BC}$ measurements (Baumgardner et al. 2012; Bond et al. 2013; Cross et al. 2010; Slowik et al. 2007). For example, the $M_{BC}$ derived from two co-located identical model filter-based light attenuation instruments under well-controlled laboratory conditions varied by more than 50 percent, and by 30 percent when compared to reference PAS measurements (Arnott et al. 2005; Mason et al. 2018; Muller et al. 2011). Inter-method variability in $M_{BC}$ increases to 80 percent when BC is embedded in or coated by other materials (Slowik et al. 2007).

Quantitative measurement of $M_{BC}$ is dependent on the establishment of suitable aerosolizable materials that mimic BC optical properties to enable instrument calibration, evaluation, intercomparison and validation. To date, a suitable material has not been developed, characterized, deployed or utilized within the aerosol community. Thus, instrument intercomparisons have been limited to studies with co-located intra-laboratory instruments measuring the same aerosol stream in parallel. Studies have focused on using BC or BC-like aerosol generated from flames which are highly variable in both $C_{abs}$ and $m_p$, impacting $MAC$, and, although not well studied, also likely impacting $MATC$ (Arnott et al. 2005; Cross et al. 2010; Slowik et al. 2007). Some studies of flame generated aerosolized materials report the
formation of highly stable, reproducible aerosol, whereas other studies cite large day-to-day variability in particle concentration and measured properties, making it a challenge to compare studies without detailed knowledge of the formation conditions, the variability of the material produced (Kirchstetter and Novakov 2007; Moore et al. 2014; Radney et al. 2013). Flame-generated materials may also contain organic aerosol (OA) and coatings of weakly absorbing organic carbon that can alter \( m_p \), and the optical and chemical properties, making them irreproducible, and unsuitable for interlaboratory studies or instrument calibration (You et al. 2016). Calibration methods have used aerosolized materials that exhibit instrumental responses mimicking a singular BC property of interest (absorption or attenuation) limiting the transferability between measurement platforms that report \( M_{BC} \) (Baumgardner et al. 2012; Bluvshtein et al. 2017; Davies et al. 2018; Laborde et al. 2012; Lack et al. 2006; Moteki and Kondo 2010; Radney and Zangmeister 2015). In addition to satisfying the above physical and chemical properties required for quantitative measurement, a BC-like reference material must also be easy to generate as an aerosol, exhibit a size distribution consistent with field-based observations (spanning mobility diameters of \( \approx 100 \) nm to \( 500 \) nm), be shelf stable, cost effective, non-toxic, and easily transferrable between laboratories (Baumgardner et al. 2012).

This study describes the characterization of a material that mimics BC optical properties and is water dispersible making it easy to transfer between laboratories and aerosolize from aqueous suspension. The particle size (i.e., mobility diameter, \( D_m \)), particle mass (\( m_p \)), and concentration (\( N \)), were measured. The material’s light absorption spectrum (\( MAC \) vs. \( \lambda \)) was measured between \( \lambda = 405 \) nm and \( 780 \) nm using particle mobility diameter (\( D_m \)) and mass-selected (\( m_p \)) aerosol. Lastly, it is demonstrated that the material can be used to measure, calibrate and evaluate photoacoustic spectrometers and filter-based instruments used to measure \( M \).
Materials & Methods

The black carbon aerosol mimic, herein termed CB, was produced by the Cabot Corporation and sold under the product trade name of Cab-O-Jet 200\(^1\) (Groves and Tuck 1979). Presented data were collected over 3 years from multiple production lots. The data was independent of production and measurement date. The elemental and chemical composition of CB were characterized using elemental carbon analysis (elemental carbon/total carbon, EC/TC) and X-ray photoemission spectroscopy (XPS). The morphology of CB was characterized using transmission electron microscopy (TEM) and by the measured mass-mobility scaling exponents (\(D_{fm}\)). The optical absorption properties of CB were characterized using photoacoustic spectroscopy and compared to filter-based attenuation measurements made using a commercially available instrument.

Aerosol generation. Aqueous CB suspensions were aerosolized using a liquid jet cross flow atomizer. Of the 2.2 L min\(^{-1}\) of flow exiting the atomizer, 0.5 L min\(^{-1}\) was sampled and conditioned by passing the aerosol laden air stream through large diameter Nafion dryer(s) and/or silica gel diffusion dryer(s) prior to measurement.

Mass-mobility exponents, effective density and mass-selected spectroscopic measurements. The use of a tandem differential mobility analyzer (DMA), aerosol particle mass analyzer (APM) and condensation particle counter (CPC) for the determination of aerosol mass to mobility diameter scaling and effective density has been previously documented (Zangmeister et al. 2014). The morphology of CB particles was ascertained from the \(D_m\) to \(m_p\) relationship using:

\[
m_p = m_{p,0} \left( \frac{D_m}{D_{m,0}} \right)^{D_{fm}}
\]  

(2)
where $m_{p,0}$ and $D_{m,0}$ represent the particle mass and mobility diameter at a reference $D_m = 250$ nm, and $D_{fm}$ represents the mass-mobility scaling exponent, a metric of particle morphology, where $D_{fm} = 2$ and 3 correspond to planar sheets and spherical particles, respectively.

The cavity ring-down spectrometer (CRD) used is identical to a previously described single wavelength CRD spectrometer, with the exception that both $\lambda = 405$ nm and 660 nm continuous wave diode lasers were used. The CRD data were collected across $\approx 3$ years (You et al. 2016; Zangmeister et al. 2018). Values of $\alpha_{ext}$ measured by the CRD were validated using $D_m$- and $m_p$-selected ammonium sulfate (AS); measured extinction cross sections ($C_{ext} = \alpha_{ext}/N$) spanning $150 \text{ nm} < D_m < 500 \text{ nm}$ always agreed with Mie theory to better than $\pm 5$ percent after accounting for density effects; see Radney and Zangmeister (2018). Notably, this level of agreement suggests that the particle counting accuracy of the CPC is also better than $\pm 5$ percent.

Aerosol were first classified by size (electrical mobility, $D_m$) using a DMA and subsequently by mass using an APM ($m_p$). The corresponding distributions of number density ($N$) and extinction coefficients ($\alpha_{ext}$) as a function of particle mass were measured using a condensation particle counter (CPC) and a CRD, respectively. The $N$ as a function of $m_p$ were then fit to a Gaussian distribution

\[
N = A_N \exp \left[ -\frac{(m_p - m_{avg})^2}{2\sigma_N^2} \right] \tag{3}
\]

where $A_N$ is the amplitude, $m_{avg}$ is the average mass and $\sigma_N$ is the 1/e halfwidth of the distribution. Particles having the same electrical mobility ($Z_p$) are selected from a distribution using a DMA. This $D_m$, defined as the diameter of a spherical particle with the same electrical mobility as those being measured, is a function of the particle’s electro-motive force (which is a function of charge) and drag force, as described by

\[
Z_p \propto \frac{q\gamma}{D_m} \tag{4}
\]
where $q$ is the net particle charge (which must be an integer), and $\gamma$ is the drag-slip correction for non-solid and/or non-spherical particles. The $D_m$ of multiply charged CB was measured using a tandem DMA arrangement where the aerosol charge was neutralized at each DMA, see Supporting Information for $D_m$ of $q = +2$, +3 CB.

The aerosol effective density ($\rho_{\text{eff}}$) was calculated from

$$\rho_{\text{eff}} = \frac{6m_{\text{avg}}}{\pi D_m^3} \quad (5)$$

In addition to data shown in the manuscript, the $m_p$ of CB as a function of suspension concentration is shown in Supporting Information.

**Mass absorption coefficient measurement.** Absorption spectra of $D_m$ and $m_p$ selected particles were measured using a single photoacoustic spectrometer (PA) utilizing both a continuous-wave diode laser ($\lambda = 405$ nm) and a supercontinuum laser with tunable wavelength and bandpass filter ($\lambda = 532$ nm, 660 nm and 780 nm), as in (Radney and Zangmeister 2015) and the Supporting Information of (Radney and Zangmeister 2017). Switching between the two lasers was accomplished using a flip optical mount. Measured 1 Hz data was averaged to 30 s from which the absorption coefficient ($a_{\text{abs}}$) was calculated; when using the supercontinuum source, wavelength regions were randomized prior to starting the measurement to avoid systematic bias from pre-ordered sets and alternated at 30 s intervals. In total, a minimum of three spectra were collected and averaged to a single replicate. For each replicate, $MAC$ at each wavelength was calculated through the second form of Eq. 1 ($MAC = a_{\text{abs}}/m_p N$). Reported $MAC$ spectra and the corresponding uncertainties represent the average values from a minimum of 3 replicates and the standard deviation of all replicates at a given wavelength, respectively.

**XPS measurements.** X-ray photoelectron spectra were acquired using a commercially available X-ray photoemission spectrometer from a thin film drop-cast onto doped silicon substrates. An
Al kα source with a 10 eV pass energy and a 90° take off angle were used. Data was collected on a single sample across several spots and elemental ratios were determined using relative sensitivity factors for each element (C 1s = 0.296, O 1s = 3.747, S 2p = 0.576).

**EC/OC Measurements.** EC/OC measurements were made using a commercially available instrument using previously described experimental conditions (Conny et al. 2003). The quartz filter was heated in an oven at 650° C to remove organic carbon prior to atomization of CB onto the filter.

**Filter measurements.** $D_m$-selected aerosol was sampled at 0.6 L min$^{-1}$ and diluted with ≈ 5.4 L min$^{-1}$ of dilution air before being transported to the filter. Size distributions were measured by a DMA-CPC as described above and shown in Fig. 1. Filter-based attenuation measurements to determine $M$ were performed utilizing size-selected aerosol at $D_m = 300$ nm. CB suspension concentration (0.25 and 0.70 mg mL$^{-1}$) was used to adjust aerosol number density at the CPC and filter-based instrument. The filter was advanced frequently to avoid shadowing effects. The delivery of $q > +1$ particles to the filter-based instrument would result increased attenuation and enhance the reported $M$ when compared to the inclusion of only $q = +1$ (i.e. attenuation of $q +2 > q +1$). This was accounted for ($N_{\text{total}} \ast m_{p,\text{total}} = N_{q=+1} \ast m_{p,q=+} + N_{q=+2} \ast m_{p,q=+2}$) by measuring the particle distribution as a function of $q$ and CB suspension concentration using a combination of tandem DMA and APM to measure the $q = +2$ mass. No $q = +2$ was detected for 0.25 mg mL$^{-1}$. The presence of $q = +2$ at 0.70 mg mL$^{-1}$ was < 4 percent in number concentration and resulted in over reporting $M$ by 6 percent, and was accounted for in reported $M$.

**Results and Discussion**

*Elemental and physical characterization of CB films and aerosol*
X-ray photoelectron spectroscopy was used to probe the interfacial elemental composition of CB thin films dropcast on doped Si wafers. Only carbon, oxygen and sulfur were detected, see Figure 2a. Elemental composition within each sample was quantified using the peak positions and intensities of the C 1s (284.6 eV), O 1s (532.0 eV), and S 2p (162 eV) using instrument and source-appropriate relative sensitivity factors for each element. The samples averaged 89.1 ± 1.7 percent carbon (1σ, standard deviation), 9.5 ± 0.7 percent oxygen and 1.8 ± 0.3 percent sulfur by mass, corresponding to an elemental ratio of C/O = 9.4 ± 0.7 and C/S = 49.5 ± 10.6. The presence of sulfur was attributed to the inclusion of the surfactant sodium 4-sulfophenylate to modify the CB particle surface and enhance its suspension in H₂O. The O 1s envelope lacks the resolution to identify specific source assignments, but was likely a combination of bound organic sulfur, surface carbon and chemisorbed, interstitial H₂O.

Carbon within CB was categorized as elemental (long range, delocalized, sp²-bound carbon) or organic carbon (sp³-bonding C-C and/or sp²/sp³-bonding C-O) using a thermal optical analyzer to detect thermally evolved carbon dioxide that is reduced to methane (CH₄) and measured using a flame ionization detector (FID). The FID response was measured as a function of sample temperature, time and gaseous atmosphere using a programmed sequence (Conny et al. 2003). Figure 2b shows the FID response as a function of time, temperature and atmosphere of CB aerosol atomized from a 1 mg mL⁻¹ aqueous suspension and collected on a quartz filter. Using this framework CB is 0.96 ± 0.05 elemental carbon (1σ).

The physical structure and morphology of CB particles were evaluated using TEM images of CB drop-cast from dilute suspension and atomized CB particles electrostatically precipitated onto lacey carbon TEM grids. CB consists of nearly spherical monomeric subunits (Figure 2c)
with an average diameter of 27 ± 7 nm (1σ) arranged into aggregates (Figure 2d) that form into nearly spherical agglomerates (Figure 2e) upon atomization at all observed \( D_m \).

**Mobility (\( D_m \)) and spectroscopic characterization of CB aerosol**

The geometric mean diameter (\( D_{geo} \)) of CB aerosol distributions and number density (\( N \)) could be controlled by adjusting the suspension concentration; size distributions were measured as a function of CB concentration from 0.25 mg CB mL\(^{-1}\) to 4 mg CB mL\(^{-1}\); see Figure 3a. The \( D_{geo} \) increased with CB suspension concentration from 169 nm at 0.25 mg CB mL\(^{-1}\) up to 233 nm at 4 mg CB mL\(^{-1}\). Despite the changes in mean \( D_m \) with CB concentration, particle mass (\( m_p \)) was only slightly affected up to 1 mg CB mL\(^{-1}\), see Figure 3b, and Figure S2 in Supporting Information. Using Eq. 2, \( D_{fm} \) was determined to be 2.83 ± 0.05 across all measured CB suspension concentrations (0.25 mg CB mL\(^{-1}\) to 4 mg CB mL\(^{-1}\)), consistent with the nearly spherical (\( D_{fm} \approx 3 \)) particles observed in TEM images. Notably, aerosol from 4 mg CB mL\(^{-1}\) had a higher mass (at constant \( D_m \)) when compared to aerosol formed at lower CB concentrations and is mirrored in the effective density (\( \rho_{eff} \)), calculated using Eq. 5, see Figure 3c. For 4 mg mL\(^{-1}\) CB suspensions, \( \rho_{eff} \) is nearly constant for \( D_m \geq 250 \) nm. At lower CB concentrations, \( \rho_{eff} \) is independent of suspension concentration and decreases nearly linearly with \( D_m \), indicating larger void volumes with increasing \( D_m \).

Spectroscopic (absorption or attenuation) determination of \( M \) requires *a priori* knowledge of aerosol optical properties (\( MAC \), and its extinction analog, \( MEC \)) as a function of \( D_m \) and \( \lambda \). For highly absorbing aerosol both \( MAC \) and \( MEC \) are likely a function of \( D_m \) and \( \lambda \) – only particles in the Rayleigh regime exhibit constant \( MAC \) and \( MEC \) – complicating the ability to quantify \( M \).
under even the most idealized measurement conditions such as a monodisperse $D_m$ and $m_p$-selected aerosol (Mishchenko et al. 1995; Moosmüller and Arnott 2009; Moosmüller et al. 2009). Thus, to enable quantification of aerosolized CB $M$, or other similar materials, the $MAC$ and $MEC$ (or other optical properties) must be known as a function of $\lambda$. Aerosol mass selection enables direct measurement of absorption on a per mass basis, as the mass absorption coefficient ($MAC$), see Eq. 1. Figure 4a shows the $MAC$ of CB as a function of $\lambda$ for $\lambda = 405$ nm, 532 nm, 660 nm and 780 nm for $m_p$-selected CB at $D_m = 250$ nm, 350 nm, and 450 nm using photoacoustic spectroscopy. The measured $MAC$ of CB was a function of both $m_p$ (or $D_m$) and $\lambda$, as shown in Figure 4b, for data collected from two separate production lots of CB. The $MAC$ decreased monotonically with $D_m$ for $\lambda \leq 660$ nm and is nearly independent of $D_m$ for $\lambda = 780$ nm; particles are closer to the Rayleigh regime so equal light penetration occurs at all $D$ (Moosmüller and Arnott 2009; Moosmüller et al. 2009). Additional spectroscopic data at $\lambda = 405$ nm and 660 nm is tabulated in Supporting Information Table S1.

The spectral shape (wavelength dependence) of absorption was also a function of $D_m$ and is quantified by the absorption Ångström exponent ($AAE$)

$$MAC_\lambda = MAC_{\lambda_{REF}} \left(\frac{\lambda}{\lambda_{REF}}\right)^{-AAE}$$

where $\lambda$ and $\lambda_{REF}$ are an arbitrary and reference wavelength, respectively. $AAE$ were calculated by fitting the absorption data at each $D_m$ to Eq. 6. The change in $AAE$ with $D_m$ is shown in Figure 4c, and shows a nearly linear decrease in $AAE$ for $D_m \leq 400$ nm and is invariant (within 1σ) at larger $D_m$. This arises from the transition of particle absorption from the Rayleigh to the Mie regime (volume to surface regime) with increasing $D_m$, as evidenced in Figure 4a (Moosmüller and Arnott 2009; Moosmüller et al. 2009; Zangmeister and Radney 2018). The measured spectral response ($MAC$ and $AAE$) of CB are both typical of highly absorbing carbonaceous
aerosol with a compacted morphology, consistent with the observed TEM images and measured $D_{\text{fm}}$ (Moosmüller and Arnott 2009; Moosmüller et al. 2009; Zangmeister and Radney 2018; Zangmeister et al. 2018).

The single scattering albedo (SSA) of an aerosol – defined as the ratio of aerosol scattering to extinction – depends on the material, morphology, $D_m$, and $\lambda$, is important in the quantification of atmospheric radiative forcing; it can change the sign of direct aerosol forcing. Well-characterized aerosol generated under laboratory conditions enables the complex parameter space in the quantitative measurement of SSA to be controlled and compared to other materials with unknown physical properties. Here, SSA was determined from the combined measurement of $MAC$ and $MEC$ (using cavity ring-down spectroscopy), see Figure 4d, for $m_p$-selected aerosol as a function of $D_m$ at $\lambda = 405$ nm and 660 nm. The $MAC$ at $\lambda = 405$ nm exhibited a nearly linear and decreasing dependence with $D_m$; a similar but smaller dependence was observed at $\lambda = 660$ nm. The $MEC$ at $\lambda = 405$ nm was nearly constant for $D_m \leq 250$ nm, and subsequently decreased with increasing $D_m$. Conversely, the $MEC$ at $\lambda = 660$ nm increased monotonically with $D_m$. The SSA at $\lambda = 405$ nm increased rapidly with $D_m$ for $D_m \leq 250$ nm, and is linear with increasing $D_m$, whereas at $\lambda = 660$ nm the SSA increases nearly linearly with $D_m$, as shown in Figure 4e. The observed spectral shape as a function of $\lambda$ and $D_m$ can be explained by the size parameter ($x = \pi D/\lambda$), as explained in detail by (Moosmüller et al. 2009) and (Moosmüller and Arnott 2009).

Demonstration of CB for instrumental and method comparison, evaluation and calibration

The spectral properties and morphology of CB closely mimic collapsed highly absorbing carbonaceous aerosol observed in aged atmospheric samples, enabling its use in evaluating techniques for determination of BC mass concentration ($M$, reported as ng m$^{-3}$). Two methods used in the measurement of $M$ are tested and compared: light absorption and filter attenuation using CB of known $m_p$ and/or $D_m$. The measurements were evaluated against $M$ determined
using a particle counter-based method \((M_C)\), where \(M_C = m_p * N\). The measurements were performed simultaneously and in parallel to ensure quantitative comparability between each technique, see Figure 1. The light absorption-based method used PAS \((M_{PAS})\) at \(\lambda = 532\) nm and 780 nm as a function of \(D_m\) using \(D_m\) and \(m_p\)-selected CB. \(M_{PAS}\) was calculated as the product of the measured absorption coefficient \((\alpha_{abs})\) at each \(\lambda\) and the measured, average \(MAC (MAC_T)\) of \(D_m\) and \(m_p\)-selected CB, \(M_{PAS} = \alpha_{Abs} * MAC_T\). Data used in \(MAC_T\) was collected and tabulated over 3 years of PAS measurements on multiple production lots of CB aerosol at NIST. Measured values of \(MAC_T\) and \(m_p\) for each \(D_m\) are shown in Table 1. The \(M_C\) and \(M_{PAS}\) were highly correlated at each \(\lambda\), see Figure 5a, with slopes of \(1.021 \pm 0.006\) and \(1.004 \pm 0.017\) (1\(\sigma\)) at 532 nm and 780 nm, respectively, illustrating that aerosolized CB can be used for \(M\) determination using \(D_m\) and \(m_p\)-selected aerosol.

The second spectroscopically-based method to test \(M\) determination measured the light attenuation of CB collected onto a filter. The filter-based method uses the measured flow rate and a manufacturer-determined \(\lambda\)-dependent mass attenuation coefficient \((MATC)\) at \(\lambda = 880\) nm to determine \(M (M_F)\) as a function of time. Mobility-only selected CB aerosol \((D_m = 300\) nm, \(m_p = 11.7 \pm 0.4\) fg) and a known and controlled flow rate of CB was delivered to the filter-based instrument and the particle counter for simultaneous determination of \(M_F\) and \(M_C\). Figure 5b shows the \(M_F\) vs. \(M_C\) across a wide, and atmospherically relevant CB \(M\) (400 ng m\(^{-3}\) to 2200 ng m\(^{-3}\)). Using this experimental scheme, \(M_F\) vs. \(M_C\) was fit using a linear function across the measured CB mass range with an intercept near the origin \((61 \pm 36\) ng m\(^{-3}\)), but \(M_F\) under measured \(M_C\) by \(7 \pm 2\) \((M_F/M_C = 0.93 \pm 0.02, 1\sigma)\) percent. It is unknown if the observed spread in the data and deviation between \(M_F\) and \(M_C\) was due to performance of the particular
instrument used in this study, or if CB’s combination of high percentage of elemental carbon, compacted morphology, and spectroscopic properties were not well captured by the instrument manufacturer MATC. As stated previously, two co-located identical model filter-based light attenuation instruments varied by more than 50 percent, suggesting that instrumental variation using factory set MATC specifications may contribute to the reported $M_F$ (Cross et al. 2010). Further investigation will be described in a follow-on paper.

Laboratories have utilized a variety of methods and materials for the calibration of aerosol photoacoustic spectrometers. Both gas phase ($\text{H}_2\text{O}$, $\text{O}_2$, $\text{O}_3$, $\text{NO}_2$) and aerosolized (nigrosin) materials have been demonstrated, using methods that are often laboratory, material, or $\lambda$ specific, limiting the transferability between measurement platforms and locations (Bluvshtein et al. 2017; Davies et al. 2018; Havey et al. 2010; Lack et al. 2006; Radney and Zangmeister 2015). Gas phase calibration of photoacoustic spectrometers is advantageous due to linking measured values to the SI using well-characterized and catalogued (HITRAN database) gas phase absorption lines with known spectral line intensity (Gordon et al. 2017; Havey et al. 2009; Long et al. 2013; Robichaud et al. 2008). Gases also require accounting for potential decomposition, contamination ($\text{NO}_2$ in $\text{O}_3$), and/or reaction ($2\text{O}_3 \rightleftharpoons 3\text{O}_2$, $2\text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_4$) and methods to deliver and quantify (e.g. CRD, hygrometer, etc.) the amount of gas delivered to the spectrometer (Bluvshtein et al. 2017). The narrow transitions of gas rovibrational lines necessitate the use of light sources that overlap the line of interest that often reside outside the spectral window (IR to nIR) relevant to BC absorption (nIR to UV). Conversely, most aerosolized materials have broad absorption features, but published values of their spectral properties are limited to a handful of materials and wavelength (Bluvshtein et al. 2017; Davies et al. 2018; Laborde et al. 2012; Radney and Zangmeister 2015; Zangmeister and Radney 2018; Zangmeister et al. 2018). A
suitable aerosol for photoacoustic spectrometer calibration across multiple laboratories would require the knowledge of the materials absorption properties ($C_{\text{Abs}}, MAC$) as a function of $D_m$, $\lambda$, and $m_p$, if possible.

The determination of CB $MAC$ as a function of $D_m$ and $m_p$ at multiple $\lambda$ may enable its use for PAS calibration. This was tested by comparison of CB and H$_2$O vapor calibrations using a previously uncalibrated photoacoustic spectrometer (combination of photoacoustic resonator and microphone) (Havey et al. 2010). The H$_2$O vapor data was collected over several consecutive days (> 10 hours of data acquisition time) due to the time required for changing and stabilizing the source. CB measurements were acquired in less than 2 hours (90 minutes of data acquisition time). The microphone signal was measured as a function of $\alpha_{\text{Abs}}$ for H$_2$O vapor at $\lambda = 725$ nm and 820 nm and using $D_m$ and $m_p$-selected CB at $\lambda = 405$ nm and 660 nm. The $\alpha_{\text{Abs}}$ of CB was determined using the second form of Eq. 1, $\alpha_{\text{Abs}} = N \ast m_p \ast MAC_T$, where $MAC_T$ at each $\lambda$ is shown in Table 1, and H$_2$O vapor calibration was previously outlined using HITRAN spectral line intensities (Radney and Zangmeister 2015). The data is shown in Figure 6 for both H$_2$O vapor and CB, where the slope ($C_S$) defines the product of the resonator cell constant and microphone responsivity (Bueno et al. 2011; Havey et al. 2010). Uncertainties in signal correspond to the standard deviation of multiple measurements while uncertainties in $\alpha_{\text{Abs}}$ represent the expanded calculated uncertainty; for RH, this includes probe precision ($\pm 0.8 \%$ RH, $\pm 0.1$ K). For CB, the uncertainty includes the combination of the measured standard deviation in $m_p$ and $N$ and $MAC$ uncertainty (see Table 1). The measured $C_S$ were $27.3 \pm 0.7$ m $\cdot$ V $\cdot$ W$^{-1}$ and $26.2 \pm 0.6$ m $\cdot$ V $\cdot$ W$^{-1}$ for H$_2$O vapor and CB, respectively, within 5 percent and 2σ of one another.
Using CB for photoacoustic calibration was more than an order of magnitude faster compared to H₂O vapor, and its use is likely only limited by the day-to-day variation of CB aerosol generation, $D_m$-selection, and $m_p$-classification. Using a similar method of classification, the measured day-to-day variation is best shown by the relative standard deviation (RSD, $= 100 \times 1\sigma/\bar{x}$) in $MAC$ at the two wavelengths used for calibration. The $1\sigma$ RSD is 6.1% and 5.5% at $\lambda = 405$ nm and 660 nm, respectively, for data collected across multiple years and CB production lots. It is reasonable that this represents an upper limit, as average the inter-day RSD of CB $MAC$ (average of 3 to 5 consecutive measurements) are 2.1% and 2.5% at $\lambda = 405$ nm and 660 nm across all $D_m$, respectively.

Using the presented data, it is possible to establish some protocols for using CB for instrument evaluation. Unless otherwise noted, the presented data was collected using a suspension concentration of 1.0 mg mL⁻¹. Using this suspension concentration and particle drying ensures comparability with the presented data. It is important to highlight that the CB spectroscopic data used for evaluation and calibration were measured using $MAC_T$ values derived from $D_m$ and $m_p$-selected aerosol. The data shown and discussed in this study should only be used with a similar aerosol classification (both mobility and mass) method to minimize the presence of multiply charged particles.

Using this suspension concentration and classification methods, it was shown that an aerosol with well characterized $\lambda$ and $D_m$ dependent spectral properties across a broad suspension concentration range enables the evaluation of instrumental response and performance, and may give guidance in the collection, reporting and quantification in future measured aerosol properties. The presented data focuses only on spectroscopic and filter-based methods. The use of CB should not be limited to these techniques and it is envisioned that CB may be used for
other techniques not investigated here where particles that mimic mature, collapsed BC may be of interest, such as evaluation of the calculated $m_p$ using particle incandescence methods (e.g. SP2) as a function of $D_m$ (Bambha and Michelsen 2015). Future investigations with CB will focus its use for interlaboratory comparability of its spectroscopic properties using $D_m$ and both $D_m$ and $m_p$-selection.

**Conclusions**

The reported data demonstrate the characterization and use of a non-toxic, water dispersible CB material with similar elemental, morphological, and spectroscopic properties to those observed in highly absorbing carbonaceous atmospheric aerosol. Using this material under well-controlled conditions enables instruments and instrumental methods to be quantitatively evaluated. This was demonstrated by comparing the measured mass concentration ($M$) of photoacoustic spectroscopy and filter-based attenuation measurements to a particle counting method. The measurements demonstrate that CB can be used to quantitatively measure method deviations. These results show that CB may be used to intercompare methods under well-controlled conditions and enable inter-method quantification of future aerosol measurements.

**References**


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Figure 1: Schematic of experimental design showing aerosol generation (black), classification (green) and spectroscopic characterization (red) where DMA = differential mobility analyzer, APM = aerosol particle mass analyzer, CPC = condensation particle analyzer, CRD = cavity ringdown spectrometer, PA = photoacoustic spectrometer. Parenthesis shows measurement performed, as described in text.
Figure 2. a) X-ray photoelectron spectrum of a drop-cast CB thin film. Designated photoemission lines shown used for determination of elemental composition. b) Flame ionization detector (FID) response (solid line) and temperature (dashed line) as a function of time (s) for $D_m$ = 300 nm CB aerosol collected on a quartz filter. Temperature and atmosphere split between organic carbon (OC) and elemental carbon (EC) denoted by vertical dotted line. c) TEM image of individual CB monomers from drop-cast aqueous suspension, scale bar is 50 nm. d) aggregates observed from dilute suspension of CB drop-cast onto TEM grid, scale bar is 200 nm. e) Atomized CB particles electrostatically deposited on lacey carbon grids. Scale bar represents 1 µm.
Figure 3: a) Particle number concentration (# cm$^{-3}$) as a function of $D_m$ (nm) atomized from 0.25 (grey), 0.50 (blue) 1.0 (red), 2.0 (green), 4.0 (black) mg CB mL$^{-1}$ aqueous CB suspensions. b) Particle mass (fg, $10^{-15}$ g) as a function of $D_m$ (nm) for 0.50 (blue), 1.0 (red), 4.0 (black) mg CB mL$^{-1}$ aqueous CB suspensions. Dashed red line represents fit of 1.0 mg CB mL$^{-1}$ aqueous CB suspension using Eq. 4. c) Effective density ($\rho_{\text{eff}}$, g cm$^{-3}$), calculated using Eq. 5 as a function of $D_m$ (nm) for 0.50 (blue), 1.0 (red), 4.0 (black) mg CB mL$^{-1}$ aqueous CB suspensions. Dashed red line represents linear best fit of 1.0 mg CB mL$^{-1}$ aqueous CB suspension. Error bars are 1σ from a minimum of 3 measurements.
Figure 4: Measured spectroscopic data for $D_m$ and $m_p$-selected CB from atomization of 1.0 mg CB mL$^{-1}$ aqueous CB suspensions. a) Mass-specific absorption coefficient (MAC) as a function of wavelength for $D_m = 150$ nm (circles), 300 nm (squares), 450 nm (triangles) mobility and mass selected aerosol, b) MAC at $\lambda = 532$ nm (green) and 780 nm (black) as a function of $D_m$. c) Ångström absorption exponent (AAE) using Eq. 6 between $\lambda = 405$ nm and 780 nm as a function of $D_m$. d) MAC (squares) and mass-specific extinction coefficient (MEC, circles) at $\lambda = 405$ nm (purple) and $\lambda = 660$ nm (red) as a function of $D_m$. e) Single scattering albedo (SSA) at $\lambda = 405$ nm (purple triangles) and $\lambda = 660$ nm (red squares) nm as a function of $D_m$. Note that ordinate are identical in a), b), and d). Uncertainties represent 1σ from > 3 measurements and 2 production lots.
Figure 5: a) Aerosol mass concentration ($M$, ng m$^{-3}$) of $D_m$ and $m_p$-selected CB measured by photoacoustic spectroscopy ($M_{PAS}$) at $\lambda = 532$ nm (green circles) and 780 nm (black squares) vs. $M$ measured by particle counting ($M_C$). Dashed line represents 1:1. Uncertainties in $M_{PAS}$ represent propagated 1σ uncertainties in $\alpha_{abs}$ and $MAC$ while uncertainties in $M_C$ represent propagated 1σ uncertainties in $m_p$ and $N$, respectively. We assume a 5% particle counting uncertainty across all $N$. b) Filter-based mass concentration ($M_F$) vs. $M_C$ of $D_m = 300$ nm CB using the manufacturer’s (default) MATC of 16.6 m$^{-2}$ g$^{-1}$ for $\lambda = 880$ nm radiation. Dashed line represents 1:1. Uncertainties in $M_F$ are ± 50 ng m$^{-3}$ for filter-based measurements and for $M_C$ the same as defined in a). Note the order of 24x difference in $M_C$ between a) and b).
Figure 6. Photoacoustic microphone signal (V W⁻¹) as a function of $\alpha_{\text{abs}}$ (m⁻¹) for H₂O vapor (black open circles) at $\lambda = 725$ nm and 820 nm and $D_m$ and $m_p$-selected CB at $\lambda = 405$ nm (open purple squares) and $\lambda = 660$ nm (open red squares). Dashed lines are linear fits of H₂O vapor (black circles) and CB data (dashed red and purple). Uncertainties in x- and y- correspond to the standard deviations of multiple measurements and expanded uncertainties in calculated $\alpha_{\text{abs}}$; see discussion in text.
Table 1. The ensemble measured $m_p$ and $MAC_T$ at $\lambda = 405\text{nm}$, $532\text{ nm}$, $660\text{ nm}$ and $780\text{ nm}$ from aqueous $1.0 \text{ mg mL}^{-1}$ CB suspension as a function of $D_m$ for aerosolized CB. Uncertainty represent $1\sigma$ of multiple measurements.

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<th>$MAC_T \lambda = 532$ nm (m$^2$ g$^{-1}$)</th>
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