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Calibration of a multi-pass photoacoustic spectrometer cell using light-absorbing aerosols

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Abstract. The multi-pass photoacoustic spectrometer (PAS) is an important tool for the direct measurement of light absorption by atmospheric aerosol. Accurate PAS measurements heavily rely on accurate calibration of their signal. Ozone is often used for calibrating PAS instruments by relating the photoacoustic signal to the absorption coefficient measured by an independent method such as cavity ring down spectroscopy (CRD-S), cavity-enhanced spectroscopy (CES) or an ozone monitor. We report here a calibration method that uses measured absorption coefficients of aerosolized, light-absorbing organic materials and offer an alternative approach to calibrate photoacoustic aerosol spectrometers at 404 nm. To implement this method, we first determined the complex refractive index of nigrosin, an organic dye, using spectroscopic ellipsometry and then used this well-characterized material as a standard material for PAS calibration.

1 Introduction

Light absorption by atmospheric aerosols still poses one of the greatest uncertainties associated with the effective radiative forcing due to aerosol-radiation interactions (IPCC, 2013). Absorption of visible incoming solar radiation exerts positive radiative forcing at the top of the atmosphere due to heat transfer from light-absorbing aerosols to their surroundings. It may also lead to stagnation and cloud dissipation (Mishra et al., 2014). In terms of positive radiative forcing, black carbon (BC) aerosols are often considered to be second only to CO₂ (Bond et al., 2013) with strong absorption throughout the solar spectrum. Characterization and quantification of light-absorbing organic aerosols, referred to as brown carbon (BrC), have been given increasing attention in the past decade (Andreae and Gelencser, 2006; Bond and Bergstrom, 2006; Alexander et al., 2008; Adler et al., 2010, 2011; Michel Flores et al., 2012; Lack et al., 2012a; Flores et al., 2014; Laskin et al., 2015; Moise et al., 2015). Although the atmospheric burden of BrC is estimated to be more than 3 times that of BC (Feng et al., 2013) its absorption is strongly spectral-dependent with strong absorption in the UV and visible (vis) spectrum and weak to non-absorbing in the longer wavelengths (Hoffer et al., 2004; Kirchstetter et al., 2004; Kaskaoutis et al., 2007; Sun et al., 2007; Chen and Bond, 2010; Moosmuller et al., 2011; Lack et al., 2012a).

Light absorption properties of BrC and its mixing with absorbing and non-absorbing aerosol components introduce a need for sensitive and accurate direct measurement of lightabsorbing aerosols in order to improve our understanding of their impact on climate. For example, filter-based techniques such as the Particle Soot Absorption Photometer (PSAP), the Multi-Angle Absorption Photometer (MAAP) and the aethalometer require correction factors which are based on some a priori information regarding aerosol type and source and have accuracy in the range of 20 to 35 % (Bond et al., 1999; Weingartner et al., 2003; Collaud Coen et al., 2010; Müller et al., 2011).

A multi-pass photoacoustic spectrometer (PAS) at several wavelengths from the UV throughout the visible spectrum has the potential to provide sensitive direct measurements of light absorption due to BrC aerosols. Coupling PAS instruments to a thermal denuder and cavity ring down spectrometers (CRD-S) to measure the absorption and extinction coefficients simultaneously at temperatures ranging from ambient to over 450 °C allows attribution of aerosol light absorption to BrC, BC and BC with enhanced absorption due to lessabsorbing coating (Cappa et al., 2012; Lack et al., 2012b).

In a PAS cell, a modulated laser light is absorbed by a sample of particles or gas, generating a modulated acoustic wave with intensity that is proportional to the energy absorbed by the sample. This acoustic wave, which is detected by a sensitive microphone, has a characteristic radial and longitudinal resonance when the light source is modulated at the cavity resonance frequency (F_r). A more detailed description of the PAS method for aerosol light absorption measurement may be found in Arnott et al. (1999) and Nagele and Sigrist (2000).

While direct, in situ aerosol absorption measurement using PAS avoids the disadvantages of filter-based techniques, an accurate calibration procedure is required to relate the instrument signal to the absorption coefficient (α_{abs}). One way of achieving this is to directly relate the α_{abs} to the microphone response and the laser power by a theoretical relation (Arnott et al., 1999):

$$\alpha_{\rm abs} = \frac{P_{\rm mic}}{P_{\rm Laser}} \frac{A_{\rm res}}{\gamma - 1} \frac{\pi^2 F_{\rm r}}{Q},\tag{1}$$

$$Q = \frac{F_{\rm r}}{\rm FWHM},\tag{2}$$

where P_{Laser} is absolute laser power in the resonator, A_{res} is resonator cross-sectional area, γ is the isobaric to isochoricspecific heat ratio taken as a constant in dry air, P_{mic} is the microphone signal power, Q is the resonant cavity quality factor and FWHM is the full width at half maximum of the acoustic response curve. The F_{r} and the FWHM are sensitive to temperature, pressure and type of carrier gas.

When the laser intensity inside the PAS cell is unknown or when it is not possible to measure, as in the case of an astigmatic cell alignment, the instrument's response needs to be calibrated empirically. This involves comparing the PAS signal to an independent transmittance measurement where scattering is negligible (Arnott et al., 2000; Lack et al., 2006). A common PAS calibration procedure is done by comparing direct measurements of α_{abs} at several concentrations of an absorbing gas by CRD-S with a parallel measurements by the PAS cell (Lack et al., 2006, 2012b; Lambe et al., 2013). This method can be applied when the Rayleigh scattering by the gas molecules is several orders of magnitude smaller than its absorption and can be neglected. Since gas-phase absorption cross sections can be highly dependent on the wavelength (Vandaele et al., 2002; Bogumil et al., 2003), it is essential to precisely know the wavelength of the light source used in each instrument or to use the same light source in both instruments.

At $\lambda = 404$ nm wavelength, NO_2 has а high molecular absorption cross section (σ_{abs}) of $6.12 \times 10^{-19} \,\mathrm{cm}^2 \,\mathrm{molecule}^{-1}$ (Bogumil et al., 2003). However, at this wavelength, NO₂ has a large quantum yield (Φ) of 0.44 (Troe, 2000) and it may readily photolyze. Without accurate determination of the laser's power, it is difficult to quantify the photolysis. At the same wavelength, O_3 has the advantage of being stable with Φ approaching zero (Bauer et al., 2000) and it can be easily produced. The disadvantage of O₃ for PAS calibration at $\lambda = 404$ nm is that its σ_{abs} is about 4 orders of magnitude lower than that of NO₂ (Fig. 1). Different studies reported a wide range of σ_{abs} for O₃ at $\lambda = 404$ nm ranging from 1.5×10^{-23} to $6.3 \times 10^{-23} \text{ cm}^2 \text{ molecule}^{-1}$ (Burrows et al., 1999; Voigt et al., 2001; Bogumil et al., 2003; Axson et al., 2011). For this reason, O₃ calibration requires very high concentration (in the order of hundreds to thousands of ppmv) which may cause equipment degradation. An additional concern is that at concentrations in the order of thousands of ppmv, O₃ may change the F_r of the PAS cell. The extent of this effect depends on the O₃ concentration and on the instruments' sensitivity to gas composition, i.e., the cell quality factor, and it can also be easily calculated using a simple thermodynamic model for the speed of sound. In such a case the laser modulation frequency should be adjusted to the new $F_{\rm r}$ value.

An alternative calibration method is to use a standard aerosol with well-known absorption properties. PAS calibration using size-selected light-absorbing particles requires a standard material with accurate information of its complex refractive index at the instrument's wavelength, which is not widely available. This procedure is also time consuming in comparison to the use of a light-absorbing gas and may be more difficult to implement in field and aircraft applications due to the need for aerosols generation and size selection equipment.

Lack et al. (2012b) reported the development of the current PAS instrument. They calibrated their PA-CRD-S (PAS coupled to a CRD-S) cells at 405 and at 532 nm with O_3 and commented that NO₂ calibration at 405 nm is possible using a photolysis correction factor for the CRD-S measurements. Several other publications used the same instruments using O_3 for the calibration procedure (Cappa et al., 2012; Lack et al., 2012a; Lambe et al., 2013).

Using a similar PAS cell as Lack et al. (2012b), we attempted to measure α_{abs} and extinction coefficients (α_{ext}) of BrC proxy materials using the PA-CRD-S following calibration of the PAS using O₃. The results yielded very high α_{abs} values which were not consistent with other measurements. Therefore, we developed a reliable procedure to calibrate the PAS instrument using light-absorbing particles produced in the laboratory with a widely available water-soluble absorbing material – nigrosin. In this study, we describe the details of this procedure, which includes high-accuracy measurement of the nigrosin complex refractive index (RI) us-



Figure 1. Spectral absorption cross sections and quantum yields of O₃ and NO₂.

ing spectroscopic ellipsometry. We also suggest that there are significant differences between the PAS response curve calculated using nigrosin particles and the PAS response curve calculated using O_3 .

2 Methodology

2.1 Photoacoustic aerosol spectrometer

The multi-pass astigmatic PAS cell that is used in this work is described in Lack et al. (2012b) and only a brief description is given here. It is composed of dual half-wavelength resonators (11 cm long, 1.9 cm diameter) capped on either end with quarter wavelength acoustic notches. The total sample cell volume is 185 cm^3 . While both resonators are open to the sample flow, only one is exposed to the modulated laser light; the other is planned for noise cancellation. Microphones are placed at the antinode of the sound wave in the center of each resonator and the speaker is placed in the background resonator.

The astigmatic optical configuration consists of two highreflectivity mirrors (ARW Optical, Wilmington, NC, USA; dielectric coating R > 99.5 %), 1.5 in. diameter, spaced 35 cm apart. The laser side mirror has a cylindrical radius of curvature of 43 cm and a 2 mm hole drilled in the center. The back mirror has a cylindrical radius of curvature of 47 cm and is rotated 90° to the radius of curvature of the laser side mirror. Astigmatic alignment is achieved by aligning the laser through the 2 mm hole drilled in the center of the first mirror and on to an off-center target on the second mirror. Each following reflection is also directed to an off-center target on the opposite mirror. Each mirror was placed on kinematic mirror mounts for easy alignment (KM200, with an AD2-1.5 adaptor; Thorlabs, USA). The PAS cell is mounted within the path of the laser multi-pass and is covered by 50 mm thick acoustic foam. The laser light passes through the PAS cell through two 1 mm thick windows (CVI Laser, Albuquerque, NM, USA), each with a high transmissivity (T > 99.5%) antireflective coating and is continuously monitored using a photodiode placed behind the back-side mirror. This is used to cancel variations in acoustic signal related to laser power fluctuations.

The $F_{\rm r}$ of the system is retrieved by producing 1 s segments of white noise using the speaker located in the reference resonator. Each segment is sampled by the microphones at a 100 kHz rate and the F_r is calculated by performing a fast Fourier transform on the measured data. Examples of power spectra with different carrier gas compositions are shown in Fig. 2, where F_r is the frequency at the peak of the fitted Lorentzian curve. Typical F_r and Q values for our instrument are in the range of 1360–1385 Hz and 40–50 (unitless), respectively, over pressure (97-101 kPa), relative humidity (RH; 0–11 %) and temperature (20 to 24 °C) ranges, and with two carrier gases (N₂ or synthetic air). The instrument described in Lack et al. (2012b) had F_r in the range of 1320 to 1360 Hz and Q in the range of 50 to 90, over pressure and temperature ranges of 20 to 90 kPa and 12 to 23 °C when dried air was used as carrier gas. Although Fig. 2 demonstrates that no change in $F_{\rm r}$ could be detected in our instrument with increasing O_3 concentration of up to 750 ppm, such a shift due to gas composition change is possible in higher Q acoustic resonator and with higher O_3 concentration.

Data acquisition and analysis is performed by sampling the microphone signal (following noise reduction) at a rate of 100 kHz and performing a lock-in calculation at the calculated Fr on a 1 s data segment. The resultant signal amplitude



Figure 2. Fast Fourier transform (FFT) resultant power spectra with different carrier gas composition and O₃ concentration. O₃ was measured downstream to the PAS using the CRD-S, assuming O₃ σ_{abs} of 1.5×10^{-23} cm² molecule⁻¹ from Axson et al. (2011).

is averaged during a single measurement duration of 2 min with standard error as the measurement uncertainty.

Linearity and validation of the PAS response is presented in the Supplement.

2.2 Cavity ring down spectrometer

A detailed description of the CRD-S method for aerosol light extinction measurement may be found in Pettersson et al. (2004), Abo Riziq et al. (2007), Smith and Atkinson (2001), Bluvshtein et al. (2012) and references therein. The CRD-S used in this study differs from the one described in a previous publication (Bluvshtein et al., 2012). Here the laser modulation rate is varied to meet the PAS cell $F_{\rm r}$. The cavity length and the aerosol filled length were extended to 95 and 80 cm respectively. The gas/aerosol inlet to the cavity was moved to the center of the cavity with two outlets at the cavity sides (Fig. 3) from which the gas/aerosols are pulled out. In this configuration, the uncertainties associated with the ratio of cavity length to aerosol filled length $(R_{\rm L})$ and purge flow dilution are reduced significantly and are independent of the flow conditions (i.e., ratio of sample flow to mirror purge flow and cavity inner diameter). Discussion on errors associated with $R_{\rm L}$ uncertainty may be found in Miles et al. (2011) and Toole et al. (2013). Additionally, N₂ mirror purge flows were maintained at $\approx 40 \text{ cc min}^{-1}$ using critical orifice with diameter of 50 µm and constant pressure difference of 12 PSI.

Data acquisition and analysis is performed by sampling the photomultiplier tube (PMT) at a rate of 10 to 100 MHz. Using an external trigger source (Fig. 3) an exponential curve is fitted to each intensity decay data set. With a laser modulation rate of 1292 to 1383 Hz (determined by PAS F_r), over 1000 decay time measurements are produced and averaged each second. The resultant 1 Hz decay time is averaged over measurement duration of 2 min with standard error as the measurement uncertainty.

Validation of the CRD-S response is also presented in the Supplement.

2.3 Photoacoustic aerosol spectrometer coupled to a cavity ring down aerosol spectrometer

The PA-CRD-S described in this section (Fig. 3) is composed of a 110 mW 404 nm diode laser (iPulse, Toptica Photonics, Germany) modulated in the measured PAS resonance frequency at 50 % duty cycle. The laser beam is split into two separate optical paths (CRD-S and PAS) using a variable polarized beam splitter. The beam splitter is composed of a quarter waveplate $(1/4\lambda)$ and a polarizing beam splitter (PBS). With the current setup, turning the $1/4\lambda$ between 0 and 90° varies the intensity ratio between the two optical paths from 0:1 to 1:1 CRD-S to PAS optical path respectively. The beam directed to the PAS is turned and aligned into the PAS cell through a set of two plano-convex lenses (focal lengths of 30 and 50 mm) used as a telescope in order to collimate the beam into a diameter of about 1.5 mm. The beam, directed to the CRD-S, passes through another $1/4\lambda$, which together with the PBS serves as a variable attenuator protecting the laser head from the beam reflected backwards by the CRD-S highly reflective mirror. This back-reflected beam (dashed arrow in Fig. 3) is transmitted through the PBS and is detected by a photodiode and is used as an external trigger source for the CRD-S intensity decay measurement. The forward beam is then turned and aligned into the CRD-S cavity by a set of turning mirrors. While the PAS sensitivity depends on the laser power, the CRD-S system requires only the minimal laser power needed by the photodiode. This allowed us to divert approximately 78 % of the laser power (about 86 mW) to the PAS cell and thus optimize its sensitivity.

2.4 Ozone production and PAS calibration

To calibrate the PAS cell, O_3 was generated by a corona discharge ozone generator (model L21, Pacific Ozone, CA, USA) with high-purity (99.999%) O_2 supplied at constant pressure (5 psi). A portion of the O_2 – O_3 outflow was diluted



Figure 3. Schematic of the photo-acoustic spectrometer (PAS) coupled to a cavity ring down (CRD) spectrometer (PA-CRD-S). Abbreviations: PBS is polarizing beam splitter; PD is photodiode; PMT is photomultiplier tube. Small black arrows indicate the entrance of the purge flows, and the thicker black arrows the direction of the aerosol flow (Bluvshtein et al., 2016).

with dry N₂ to a 90% N₂ 10% O₂–O₃ mixture. O₃ concentrations were varied by adjusting the voltage gauge of the corona discharge generator. In addition, a UV lamp O₃ generator (model 300, Jelight Company, Inc. CA, USA) was also used to calibrate the PA-CRD-S with a constant flow of 0.1 L min⁻¹ high-purity O₂ for O₃ concentration of up to 800 ppm. In this case O₃ concentrations were varied by adjusting the height of the cover glass.

Contamination by NO₂ could occur under corona discharge if N₂ and water vapor are present. Even at low concentration NO₂ may induce significant calibration errors because its absorption cross section is about 4 orders of magnitude larger than that of O₃ and because it is expected to undergo photolysis in the PAS cell where the laser power is significantly higher than in the CRD-S. In order to avoid NO₂ contamination only high-purity, dry gases were used.

Several different instrumental setups were used to test the robustness of the O_3 calibration. In a tandem setup $0.6 \,\mathrm{L\,min^{-1}}$ of the 90 % N₂ 10 % O₂–O₃ gas mixture was flown first through the PAS cell followed by the CRD-S (and vice versa). With the tandem setup the CRD-S was used without mirror purge flows and with side inlet and outlet. In a parallel setup, the gas mixture flow was pulled and split between the PAS and the CRD-S at flows of 0.6 and 0.2 L min⁻¹, respectively, to equal the volume ratio of the two instruments. In the parallel flow configuration gas was pulled into the CRD-S through the center inlet and pulled out through the side outlets while the mirror purge flows were used. Constant flows were maintained by three mass flow controllers (one for the PAS and one for each cavity out flow of the CRD-S).

All of the flow lines and tube connectors exposed to O_3 were 1/4 in. Teflon tubing and the flow line between the instruments (for the tandem setup) was 10 cm long.

2.5 Measurement of the complex refractive index of nigrosin by spectroscopic ellipsometry

Water-soluble nigrosin is the sodium salt of the sulfonation product of spirit-soluble nigrosin, which is a mixture of black dyes widely used in life science research for negative cell staining. Water-soluble nigrosin (nigrosin; hereafter) was also previously used as a model material for highly lightabsorbing aerosols (Lack et al., 2006; Michel Flores et al., 2012). The chemical structure and optical properties of nigrosin are poorly characterized and may differ between lot due to the nature of the production protocol. To infer the complex RI of nigrosin at $\lambda = 404$ nm from spectroscopic ellipsometry (SE) measurements, five silicon wafers (surface area of 4 cm^2) with 300 nm of silicon thermal oxide (Virginia Semiconductor, VA, USA) were coated with nigrosin (Sigma-Aldrich, lot number: 14828BD) using concentrated aqueous solutions and a spin coater (WS-400A-6NPP/LITE; Laurell Technologies Corporation, PA, USA). The concentration of the nigrosin solution was 1.25 and 1.5 times the room temperature solubility limit of nigrosin (10 g L^{-1}) and was kept at 40 °C under constant stirring to maintain solubility. Spin coating was done in two stages, a coating stage and a drying stage. During the coating stage, each sample was covered by the nigrosin solution and the spinning was done at 100, 500 or 700 rpm under dry N₂ flow for 14 min. The drying stage was performed at 3500 rpm for 1 min in order to reach complete dryness and to remove liquid droplets adhering to the wafer edges. Dry N2 flowed from below the wafer stage in an upward direction so it will not affect the liquid spreading on the wafer.

Spectroscopic ellipsometry is a proven method to determine thin film thickness and complex refractive index (m = n + ik) of materials (Fujiwara, 2007). Briefly, ellipsometry uses polarized light to characterize thin film and bulk materials. A change in the electric field amplitude and phase for p

Parameter	Precision	Accuracy	Total
Laser wavelength	_	$0.5\mathrm{nm}^1$	0.5 nm
Particle diameter	_	-	$10 \%^2$
Size distribution	-	_	$20 \%^2$
Bin height			
Particle number	$pprox$ 0.3 $\%^4$	$10 \%^{3}$	\approx 10.3 %
Concentration			
Complex refractive	5	_	_
Index			

Table 1. Uncertainty on the Mie routine input parameters used to calculate the absorption coefficient of the size-selected nigrosin (and SRFA and PPFA) particles.

¹ Spectrometer resolution. ² Buonanno et al. (2009), Fig. 2. ³ TSI Inc.

⁴ Calculated standard error. ⁵ Retrieved from SE analysis.

and s polarizations is measured after reflecting light from the surface. Thin film thickness and optical constants (n and k)are derived from the measurement. Spectroscopic ellipsometry measurements were performed on the five film samples (described above) using a J.A. Woollam M-2000 DI ellipsometer in the spectral range of 193 to 1700 nm at angles of incidence of 55, 65 and 75°. The instrument was precalibrated with a calibration wafer to minimize systematic errors that are related to angle, wavelength and delta offsets. In case of light-absorbing materials, k is often correlated with the sample thickness. To overcome this issue, we employed the interference enhancement technique to improve sensitivity to light absorption as described in Hilfiker et al. (2008). The resulting film optical constants were evaluated by comparison with the optical constants obtained from a simultaneous analysis of all five samples (multi-sample analysis; MSA). With the two methods, we obtained high sensitivity to light absorption. The Kramers-Kronig consistent complex refractive index of the nigrosin films was modeled using five Gaussian oscillators along with a Sellmeier function. The best-fit model was determined by the Levenberg-Marquardt regression algorithm and tested for both statistical errors and model systematic errors. Statistical errors were estimated by the bootstrap resampling method (Rosa, 1988) and the model systematic errors were estimated using the difference between the measured data and the best-fit model generated data.

2.6 PAS calibration with measurements of nigrosin aerosol

A nigrosin solution was atomized and the resulting aerosol dried (RH < 10%) and size selected (Bluvshtein et al., 2012; Michel Flores et al., 2012). Selected diameters ranged from 250 to 325 nm (at 25 nm steps), and the absorption signal was measured with the PAS instrument at several number concentrations (varying from 200 to 1500 particles cm⁻³) counted by a condensation particle counter (CPC, 3775, TSI, MN, USA). Size selection was performed using an electrostatic



Figure 4. Complex RI results of spectroscopic ellipsometry measurements of nigrosin coating on Si oxide. Also shown are the results of an imaginary part calculated from aqueous UV–vis measurements based on Sun et al. (2007) with a density value of 1.6 g cm^{-3} (Moteki et al., 2010). The range of the shaded area is the sum of the variance of the absorption measurements (about 2 to 5%) and 5% uncertainty on the reported density measurement technique (McMurry et al., 2002).

classifier (3080L, TSI, MN, USA) equipped with an impactor (nozzle diameter of 457 µm). Sample flow was set between 1 to $0.7 \,\mathrm{L\,min^{-1}}$ such that the 50 % cutoff diameter of the impactor was 50 nm above the selected size (additional details are provided in the Supplement). The impactor was used to reduce multiply charged particle (MCP) contribution. $0.6 \,\mathrm{L\,min^{-1}}$ were pulled through the PAS cell and evenly split between the CPC $(0.3 \,\mathrm{L\,min^{-1}})$ and the CRD-S. In this setup, the CPC measurement could be applied to both instruments (PAS and CRD-S) without correcting for particle loss. Flow line lengths downstream of the PAS were kept to minimum and were composed of 1/4 in. outer diameter conductive tubing to minimize particle loss due to electrostatic adhesion. PAS and CPC data were acquired at 1 Hz for 120 s and used as averaged with standard error to describe their uncertainty. The aerosol α_{abs} was calculated using Mie theory algorithm with the complex RI (retrieved from the dry film SE measurements), particles number concentration and a log-normal size distribution function (with geometric standard deviation of 1.1) to simulate the DMA transfer function of the singly charged particles, as input. Uncertainties in input values were propagated through the calculation (Table 1). The calculated aerosol α_{abs} was then plotted against the PAS signal in order to retrieve the nigrosin particles calibration curve.

3 Results

Figure 4 shows the result of a single sample and a MSA of the spectroscopic ellipsometry complex RI retrieval, at 300 to 800 nm range. The single sample analysis shown was performed on the sample with the thickest retrieved nigrosin film $(137.2 \pm 0.3 \text{ nm}, \text{ coated with } 15 \text{ g L}^{-1} \text{ nigrosin solution})$ at 100 RPM). The RI values derived by the SE analysis are listed in Table S1 of the Supplement. The imaginary part from the SE analysis is in good agreement with the imaginary part calculated from UV-vis absorption measurements of aqueous solutions (Sun et al., 2007) with mass concentrations of 6.25, 16.67, 25, 33.33 and 50 mg L^{-1} . The density of nigrosin for this calculation was taken as $1.6 \,\mathrm{g \, cm^{-3}}$ (Moteki et al., 2010) with 5% uncertainty (McMurry et al., 2002). The complex RI of nigrosin at $\lambda = 404$ nm was determined by spectroscopic ellipsometry to be m = 1.624 $(\pm 0.006) + i \ 0.154 \ (\pm 0.008)$. The summed precision and accuracy of the retrieved complex RI is $\approx 0.4\%$ for n and \approx 5 % for k. Figure 4 also shows previously published complex RI values for nigrosin retrieved at 532 nm and 355 nm wavelengths using CRD-S (Lack et al., 2006; Dinar et al., 2008; Lang-Yona et al., 2009; Bluvshtein et al., 2012; Michel Flores et al., 2012). Such widespread of complex RI values emphasizes the need for more accurate measurements for future use of nigrosin as a standard material and the limitations of the CRD-S method, which can benefit from a new wellestablished standard.

Figure 5 shows O₃ calibration curve where the corona O₃ generator was used with a "PAS first" tandem instrumental setup of the PA-CRD-S. The O₃ concentration (inferred from the CRD-S absorption coefficient) ranged from 250 to 1900 ppm. Linear regression produced a slope of $4.975 \times 10^{-7} \text{ cm}^{-1} \text{ V}^{-1}$ with uncertainty of about 0.01 %, demonstrating the appeal of gas-phase calibration of PA-CRD-S systems. The low uncertainty of the fitted curve originates from the high dynamic and linear range of the system and its stability with gas-phase measurements.

The differences in O_3 calibration slope between the different setups, which were below 5 %, and results of additional tests discussed further in the Supplement emphasize that no significant NO₂ contamination was present in the corona discharge ozone generator.

Also shown in Fig. 5 is an aerosol-phase calibration curve produced with size-selected nigrosin particles described in the methodology section. The absorption coefficients associated with these measurements were calculated using the Mie routine with the complex RI retrieved from the SE analysis. Linear regression produced a slope of 2.554×10^{-7} cm⁻¹ V⁻¹ with uncertainty of about 4 %, which mostly depends on the magnitude of errors propagated through the calculation (Table 1). The about 2-fold difference between the two calibration techniques cannot be resolved by a more conservative error estimation of the Mie routine input variables. Moreover, for the PAS measurements of the

nigrosin particles to satisfy even a weak agreement with the O₃ calibration curve, assuming homogeneity and sphericity of the measured nigrosin particles, their complex RI would need to be about m = 2.3 + i0.4 (form Mie theory calculation in the complex RI range of 1.3 < n < 2.8 and 0 < k < 1.5) which is highly unlikely.

To test the effect of possible underestimation of nigrosin complex RI from the SE analysis we used the Bruggeman effective medium approximation (EMA; Aspnes, 1982) and assumed air voids trapped in the thin nigrosin film. The film was treated as a homogenous mixture of nigrosin with unknown complex RI and air with m = 1 + i0 and the original SE measurement of the single sample was reanalyzed with air voids volume fraction increasing from 0 to 20% in 0.5 % intervals and a new complex RI for "pure" nigrosin was retrieved. The nigrosin calibration curve for the PA-CRD-S system was then calculated for each new complex RI. Figure 6 shows that as the air voids volume fraction increases the retrieved complex RI of nigrosin also increases with a much more significant effect on the real part. The resultant aerosol calibration slope increases as expected but is still significantly smaller than the O₃ calibration slope. Note that as the calibration slope increases the "goodness" of the linear fit is reduced (χ^2 increases), which means that the complex RI used in the calculation is less probable to represent the measured nigrosin particles.

To further verify the validity of the new calibration approach we have used Pahokee peat fulvic acid (PPFA) and Suwannee river fulvic acid (SRFA) which are often used as a proxy material for atmospheric BrC due to their complex organic composition and their UV–vis absorption spectrum. In an accompanying paper Bluvshtein et al. showed that the mass absorption cross section (MAC) of PPFA and SRFA, calculated from UV–vis aqueous solution absorption spectrum, is within the range of MAC values calculated for ambient water-soluble organic aerosol collected during a biomass burning event.

Size-selected PPFA and SRFA particles were measured with the PA-CRD-S and the complex RI was retrieved from the CRD-S measurements using a Mie theory algorithm, taking into account the MCP contribution (Michel Flores et al., 2012; Washenfelder et al., 2013; Bluvshtein et al., 2016). The imaginary part of the complex RI was also calculated from UV-vis aqueous solution absorption measurement using material density estimation of 1.1 to $1.3 \,\mathrm{g}\,\mathrm{cm}^{-3}$. From these measurements, we have compiled our best estimation of the complex RI of PPFA and SRFA at $\lambda = 404$ nm as $m = 1.699 \ (\pm 0.012) + i \ 0.036 \ (\pm 0.010)$ and m = 1.685 $(\pm 0.020) + i \ 0.013 \ (\pm 0.010)$ respectively. This information, together with the measured particle number concentration and calculation of the MCP contribution, was used to calculate the α_{abs} using Mie theory. Calculated α_{abs} values of PPFA and SRFA are also plotted against the measured PAS signal in Fig. 5 with slopes of $2.181 \times 10^{-7} \ (\pm 14 \ \%)$ and $2.554 \times 10^{-7} \ (\pm 35 \ \%) \ cm^{-1} \ V^{-1}$ respectively. Figure 5



Figure 5. PAS O_3 calibration curve and regression (gray), nigrosin calibration curve and regression based on SE analysis (black circles and line) and PPFA and SRFA based on complex RI retrieval from CRD-S measurements and aqueous UV–vis measurements. Absorption coefficients for the nigrosin, SRFA and PPFA were calculated using Mie theory routine.



Figure 6. (a) and **(b)** Complex RI of the "pure" nigrosin component, reanalyzed from SE measurement, assuming a mixed nigrosin–air film with increasing homogenous air voids fraction. **(c)** Calculated PA-CRD-S nigrosin, aerosol-phase calibration slope and **(d)** associated χ^2 value.

clearly demonstrates that the PAS response curves calculated for the three types of organic aerosols agree with each other, while the slope of the response curve produced with O_3 overestimates the instrument's response by a factor of about 2. This implies that measurements of aerosols α_{abs} at $\lambda = 404$ using similar PAS instruments calibrated with O₃ may be significantly overestimated.

We note that the uncertainties on the linear regression slopes of PPFA and SRFA are significantly larger than that of the nigrosin particles due to significantly larger uncertainties on the complex RI. This emphasizes the added value of the SE analysis.

Possible reaction of the O_3 with residual aerosol material on the walls of the instruments will produce ultra-fine lightscattering particles. These particles, if produced, would increase the CRD-S α_{ext} and cause an overestimation of the calibration slope. However, this effect is expected to reduce the stability of the CRD-S signal during the gas-phase measurement and is also expected to change over time, which will lead to nonlinear calibration slopes calculated from prolonged calibration procedure or at least significant difference between different calibrations. From repetitions of the calibration procedure in tandem and parallel flow configurations, linearity and repeatability of the calibration curves, and the stability of the CRD-S signal we concluded that this effect is unlikely to cause the overestimation of the PA-CRD-S O_3 calibration curve.

This claim is supported by compering CRD-S α_{ext} measurement of the O₂/O₃ gas from the UV lamp generator with the concentration given by the O₃ monitor (following 10-fold dilution with dry N₂). This yielded σ_{abs} for O₃ molecule of about 1.8×10^{-23} cm², which is in the range of recent publication (Bogumil et al., 2003; Axson et al., 2011). Increased α_{ext} due to newly formed particles would cause overestimation of σ_{abs} of O₃ molecules.

Additionally, we did not find any information in the literature regarding non-thermal energy relaxation processes following UV–vis light absorption by O_3 .

4 Conclusions

In this study we propose a new calibration scheme for astigmatic PAS instrument using nigrosin, a widely available water-soluble absorbing material. We have derived the complex refractive index of nigrosin (Sigma-Aldrich, lot number: 14828BD) throughout the UV and visible range using spectroscopic ellipsometry and suggest that it can now be used as a standard material to calibrate PAS instruments at the UVvis wavelength range for measurements of light-absorbing aerosols. Although nigrosin can also be used to validate other PAS calibration procedures, we recommend that, if nigrosin from a different lot or supplier is used, a detailed analysis of its optical properties be compared to our results.

As shown in this study, spectroscopic ellipsometry can be used to accurately determine the complex RI of other organic dyes that may be used for the same purpose. It requires, however, the production of uniform films of the studied material.

Our measurements also imply that calibration of PAS with O_3 at 404 nm can possibly lead to overestimation of light absorption by aerosol. However, there remains an uncertainty as to the origin of this observation. We suggest that further research of this issue in a similar system will be beneficial.

PA-CRD-S calibration using light-absorbing aerosols may be difficult in a field campaign or on board an aircraft. For this reason we suggest comparing O_3 calibration curves to light-absorbing aerosols calibration curves in the laboratory at different pressure and temperature conditions. In this way it is possible that O_3 calibration curves can still be applied and corrected under such operating conditions.

Data availability. For data related to this paper contact Yinon Rudich (yinon.rudich@weizmann.ac.il).

The Supplement related to this article is available online at doi:10.5194/amt-10-1203-2017-supplement.

Competing interests. The authors declare that they have no conflict of interest.

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