

Response to Anonymous Referee #1 comments (RC1) on

A novel approach to calibrating a photo-acoustic absorption spectrometer using polydisperse absorbing aerosol (<https://www.atmos-meas-tech-discuss.net/amt-2018-413/>)

We found the comments from referee #1 to be highly valuable and the paper has been improved because of this diligent review. We have carefully edited the manuscript and we believe the “sloppy” or “draft” feel of the manuscript has been corrected. We believe, given that Anonymous Referee 1 stated that the data analysis “looks solid”, that there is not a need for re-submission, but rather that the significantly corrected/improved manuscript submitted to the editor is ready for publication in AMT.

Please note that page and line numbers listed below refer to the locations in the original manuscript posted in AMTD.

Comment #1:

This manuscript has a “draft” feel to it. While the data analysis looks solid there are passages in the manuscript that can only be described as sloppy and as such warrants better and more clear writing. I draw your attention to three examples of this. First, the authors cite that “the precision of filter-based measurements is considered to be roughly 30-35%” (page 2, lines 19 & 20). This is wrong (and sloppy) as the PSAP has outstanding precision. Where the PSAP fails is in accuracy as the various correction schemes used to remove measurement bias directly impact the accuracy of the measurement - not its precision. Accuracy is what Bond et al., (reference cited by the authors) also refer to.

Response to comment #1: We are grateful to the referee for pointing out these errors in the language used. We have gone through the manuscript carefully to ensure there are no further “sloppy” errors and have made a number of changes. Specific to this comment, we have replaced “precision” with “accuracy”.

P2,L19 now reads: “While filter-based measurements can have high precision, absorption measurements made by filter-based measurements are typically only accurate to within roughly 30-35% (Bond et al., 2013).”

Comment #2:

Second, when discussing the PSAP the authors make reference to the “attenuation of laser energy” (page 2, line 15). This is wrong as the PSAP does not have a laser (it uses LEDs).

Response to comment #2: This was indeed a sloppy typo to reference the laser attenuation of a PSAP, when in fact the PSAP uses LEDs.

This sentence now reads (P2,L15) “These approaches utilize a measurement of the attenuation of light intensity (typically from an LED) due to absorption by aerosols that are captured on a filter, but these techniques are prone to a variety of biases from multiple scattering within the filter itself, variability in backscatter based on the size distribution of the particles, and issues with non-linear responses to loading as the filter becomes saturated (Bond et al., 1999; Collaud Coen et al., 2010; Kondo et al., 2009; Lack et al., 2014; Müller et al., 2011; Weingartner et al., 2003).”

Comment #3:

The statement written on page 5 lines 28-30 “Three different absorbing substances were used in this study: Aquadag, Nigrosin, and Regal Black. All three are commonly used to generate absorbing aerosol for optical measurements or for measurements by the single particle soot photometer (SP2)”. This is very misleading, for one could easily infer that nigrosin is used with the SP2, which is certainly not the case.

Response to comment #3: We agree that the sentence was, unintentionally, misleading and we agree that the SP2 generally uses Aquadag or Fullerene Soot, and not Nigrosin or Regal Black, to calibrate. This part of the paper has been augmented now to be accurate by stating that the three substances are commonly used to generate absorbing aerosol for optical measurements by photoacoustic absorption spectrometers, and Aquadag is commonly used for measurements by the single particle soot photometer (SP2).

New sentence beginning P5,L28: “All three are commonly used to generate absorbing aerosol for optical measurements by photoacoustic absorption spectrometers, and Aquadag is commonly used for measurements by the single particle soot photometer (SP2) (Baumgardner et al., 2012; Gysel et al., 2011; Jordan et al., 2015; McMeeking et al., 2014; Saleh et al., 2013).”

Comment #4:

While this reviewer agrees with the authors stated toxicity concerns of NO₂ based calibration, it should be noted that typical concentrations used to calibrate this class of instrumentation are in the 10s - low 100s of ppb range - a range that is easily and safely used in laboratory and field conditions. The big issue for NO₂ is our uncertainty with respect to photodissociation at 405 nm and thereby limiting the utility of this gas at this wavelength. In contrast, this gas standard remains a very good (best?) calibration at 532 nm.

Response to comment #4: The authors appreciate this input and clarification from the reviewer. The paragraph the reviewer is referring to has now been improved because of this comment.

P3,L12 now reads: “The primary problem with using NO₂ to calibrate is that NO₂ photolyzes at 405 nm and the magnitude of photolysis depends on the laser power in the instrument (Jones and Bayes, 1973; Lack et al., 2012a), so while it would be a good calibration standard at 532 nm, it is a poor standard near or below 405 nm. Even for 532 nm cells, calibration with NO₂ requires exact matching of laser wavelengths between the PAS and CRDS, has the potential for reactive loss, and requires the use of a toxic substance. While the NO₂ concentrations are often small enough not to pose a significant health hazard, NO₂ use on airborne platforms still requires significant additional safety precautions.”

Comment #5:

The 405 nm calibration curves shown in Figure 5 for both Regal black and Aquadag give intercepts of 11.24 Mm⁻¹ and 5.5 Mm⁻¹, respectively. Do the authors have an explanation for non-zero intercepts? In the atmospherically-relevant range for aerosol absorption (0-25 Mm⁻¹) such an offset is huge. It is interesting to note that the intercept for nigrosin is < 1 Mm⁻¹. A similar trend is seen at 660nm.

Response to comment #5: The authors thank the reviewer for raising this question, and the matter has been revisited and carefully considered. The calibration method uses 5 different concentrations, and for the regal black (the substance with the largest intercept), the largest concentration is 600 Mm⁻¹, while the smallest is 36 Mm⁻¹. The slope is therefore calculated with the accuracy stated in the paper, but the intercept is not used as part of the calibration and can be significantly off because the larger concentrations control the slope. To apply the calibration in field or laboratory measurements, we use a filter period to determine zero and then apply our slope from the most recent calibration to signal above this zero level. Were we to include filter data or low concentration points, the intercept would be shifted down to near the origin. In fact, forcing the line to go through the origin alters the slope by only 3% in this particular case. We feel it is best not to force the fit through zero to obtain the best slope, but the slope would not shift dramatically regardless.

We have added the following sentences at P8,L31: “In practice, the calibration slopes are applied to the PAS microphone signal to convert from integrated area to absorption (as outlined in section 2.1). Filter

periods are frequently conducted to determine the background absorption and the PAS data is zeroed to this background. Large (on the order of several hundred Mm^{-1}) concentrations are used to generate a slope that can be applied over significant concentrations in field measurements of smoke particles. Therefore, intercepts can be on the order of 10 Mm^{-1} . The intercepts from the calibrations are not used.”

Comment #6:

This reviewer would like the authors to provide some cautionary text regarding extrapolation of measurements/data collected at 450 nm (CAPS) to 405 nm (PAS). Yes, the results seem to suggest all is fine, but this may be a fortuitous and be a unique case. Indeed, as the authors point out, the standard deviation for nigrosin is significantly larger (3-5x) than the other two calibration standards examined. This larger uncertainty for nigrosin could be due to manufacturers mixing the polyaniline nigrosin pigment (which is bluish/black color) with an orange dye in order to achieve a specific color index (CI: 50420) which could lead to a very different wavelength dependence that is captured between the CAPS wavelengths and that could, in turn, easily cause an error at the extrapolated wavelength of 405 nm.

Response to comment #6:

We agree that the method of using absorption angstrom exponent to relate absorption at 450 nm to absorption at 405 nm can be problematic for certain substances. Based on this comment and others from the reviewers, we have expanded Section 3.2 to make the case for using regal black or aquadag rather than nigrosin, given that nigrosin’s absorptivity has a complicated dependence on wavelength. We note, however, that even for Nigrosin, shifting absorption from 450 nm and 405 nm via AAE introduces only a 3% bias.

P8,L4 has been adjusted and now reads: “Nigrosin has been shown to have an index of refraction that varies across the visible wavelengths (Bluvshstein et al., 2017), and does not have a relationship between absorption and wavelength that is perfectly modeled by AAE. However, given that the adjustment is only over a small wavelength range, the error introduced by adjusting absorption measurements from 450 to 405 nm with the AAE technique is assessed here.”

Comment #7:

The authors may consider putting several of the figures in a supplemental section and limit main figures to those that are most germane to the manuscript subject matter (e.g., figures 2, 5 and 7).

Response to comment #7: While we appreciate the desire for brevity, after considering the matter and noting that this is a technique paper, we believe it’s appropriate to leave the other figures that show the experimental setup, an example of raw data, instrument noise levels and error analysis. Accordingly, we have decided to maintain the current structure of the paper and keep all figures in the main body. A supplement has been created to include the figures requested below in comments 8 and 9.

Comment #8:

It would be nice to see actual aerosol size distributions for the samples used in these experiments (page 6, lines 1-6). This is a figure that could be shown in the aforementioned supplemental section.

Response to comment #8: Aerosol size distributions corresponding to the data displayed in figures 3 and 5 has been provided in SI figure 1. The new supplementary material is provided at the end of this document.

Comment #9:

This reviewer would also like to have seen some SSA plots from the actual calibration materials used and currently limited to the pure scattering experiments.

Response to comment #9: SSA data from the experiments shown in figures 3 and 5 can now be found in SI Figure 2.

Response to anonymous referee #2 comments (RC2) on

A novel approach to calibrating a photo-acoustic absorption spectrometer using polydisperse absorbing aerosol (<https://www.atmos-meas-tech-discuss.net/amt-2018-413/>)

The authors greatly appreciate the comments, corrections, and suggestions from this anonymous referee. Please note that the individual responses for each comment below use the page and line numbers from the manuscript that was originally submitted in AMTD.

Comment #1:

Typical analyses of photoacoustic data have included the effect of the acoustic frequency, quality factor of the acoustic cavity, and laser power. Even if these quantities are constant for these experiments, the authors should include them in their formalism. Generally some more formalism such as the photoacoustic equation relating microphone signal to absorption coefficient would be a benefit.

Response to comment #1:

In the portion of the introduction that discusses photoacoustic spectrometry history and the different calibration approaches, the authors have added a discussion of the photoacoustic equation and the equation itself. These additions are

P3L1: “Theoretically, the absorption (b_{abs}) coefficient can be determined from a PAS as a function of absolute laser power (P_{Laser}), pressure at the microphone (P_{Mic}), resonator cross sectional area (A_{Res}), resonant frequency F_R , and quality factor (Q).

$$b_{abs} = \frac{P_{Mic} A_{Res} \pi^2 F_R}{P_{Laser} \gamma - 1 Q} \quad (1)$$

For multi-pass instruments it is difficult (Fischer and Smith, 2018b) or not feasible given the instrument setup (Lack et al., 2012b) to know all of these terms accurately. This means the first principles approach of Arnott et al. (1999) is not possible for many instruments. The issue with a fundamental calibration is that the overlap integral of the laser, acoustic mode, and aerosol is not known accurately enough for calibrations. Additionally, the microphone sensitivity and laser power are not known accurately enough for calibration purposes in the design of Lack et al. (2012b).”

Comment #2:

The typical style is to leave a space between quantity and the unit. Please check this, in particular when wavelengths are reported.

Response to comment #2: The authors apologize for this error and appreciate the attention to detail from the referee. All such cases of a space missing have been found and corrected. Listed are the locations where a space needed to be added between the wavelength and unit:

p1L17;p3L21;p4L13;p6:L5,L24,L29,L31,L32;p7L10;p8L7,L29,L30;p10L2,L3,L10,L11,L12

Comment #3:

Some values and errors are reported with too many significant digits

Response to comment #3: The authors have carefully gone through the manuscript to confirm consistency of significant digits between values and errors within each analysis. Several cases of

excessive significant figures were found and have now been altered (P10L11,P10L13,P10L15,P10L31). This comment from the referee is much appreciated.

Comment #4:

The optical power in these multipass cells is not unknowable. It can be determined with few simple measurements. 1) Measure the transmission of the rear mirror. 2) place a calibrated optical power meter to measure the optical power leaking through the mirror. 3) account for the mirror transmission and a factor two for a similar amount of light leak through the front mirror to get the optical power in the acoustic cavity. The issue with a fundamental calibration is that the overlap integral of the laser, acoustic mode, and aerosol is not known accurately enough for calibrations. Or possibly the microphone sensitivity and/or the laser power are not known accurately enough for calibration purposes.

Response to comment #4:

We agree that the issues were oversimplified in the AMTD manuscript. We have adopted to reviewer's suggestion and the passage on P3L1 now reads: "For multi-pass instruments it is difficult (Fischer and Smith, 2018b) or not feasible given the instrument setup (Lack et al., 2012b) to know all of these terms accurately. This means the first principles approach of Arnott et al. (1999) is not possible for many instruments. The issue with a fundamental calibration is that the overlap integral of the laser, acoustic mode, and aerosol is not known accurately enough for calibrations. Additionally, the microphone sensitivity and laser power are not known accurately enough for calibration purposes in the design of Lack et al. (2012b)."

Comment #5:

P3L23: 'area' should be 'are'

Response to comment #5: corrected

Comment #6:

P4L11: extra space before "Lack"

Response to comment #6: corrected

Comment #7:

P4L19: Because this acoustic cavity consists of two high coupled resonators, there are two "primary" eigenmodes. In one mode the pressures at center of both resonators are in-phase and in the other the pressures are 180 deg. out of phase. Please rewrite the sentence to clarify which mode is being used.

Response to comment #7: Thank you for this input, this sentence has been reworded to explain that in our instrument, the antinodes are at the center of each cell and are 180 degrees out of phase.

P4L19: "The primary eigenmode of this instrument consists of one full wavelength across the two cells, such that the antinodes are at the center of each cell and 180 degrees out of phase."

Comment #8:

P5L4: either "each cell's resonant frequency" or "each cells' resonant frequencies" would be appropriate.

Response to comment #8: We appreciate this attention to detail. Pertaining to both this comment and comment #9, this sentence now reads:

“To obtain the maximum and consistent signal the lasers must be modulated at each cell’s resonant frequency, which is dependent on temperature and pressure in the cell. Accordingly, a resonant frequency calibration is performed at regular intervals (typically at least every 5 minutes), to account for any drifts in temperature or pressure.”

Comment #9:

P5L5: please replace “whatever interval” with a more formal phrase

Response to comment #9: Thank you, the sentence has been corrected with “a regular interval”, and we clarify that we have not set a specific timing, but this frequency calibration is done at least every 5 minutes. See above for the new sentence.

Comment #10:

P5L6: The microphone part number does not need to be repeated here.

Response to comment #10: corrected

Comment #11:

P5L15: track changes indicator on this line

Response to comment #11: corrected, thank you

Comment #12:

P6L2-6: If known please state the concentration of solution that is used. Even if it is not critical, it is a good starting point for future projects and replication.

Response to comment #12: The starting amounts of Nigrosin/Regal Black/Aquadag were not recorded due to the variability between tests and the need to add substances or serially dilute. However, we have added an indication of the amount of substance that was initially added and the amount of water that was initially used.

P6L2: “A few crystals (solids) or a quarter spatula (slurry), of the given substance is mixed with Milli-Q water (Millipore system SimPak2) and progressively diluted (starting with a couple hundred ml of water) until the size distribution of the atomized aerosols is such that 99% of the mass is below 300 nm. More dilute solutions tend to yield aerosol with smaller sizes.”

Comment #13:

P6L21: in this sentence please replace the ‘extinction’ with ‘extinction channel’

Response to comment #13: corrected

P6L30: “The scattering channel for the CAPS PM_{SSA} is calibrated relative to the extinction channel, because the extinction does not require calibration.”

Comment #14:

P7L25-30: Nigrosin has a complex absorption spectrum and is not appropriately modeled with an angstrom exponent model.

Response to comment #14: The authors agree that Nigrosin does not follow the relationship between wavelength and absorption modeled by an angstrom exponent. The discussion in section 3.2 has been modified to add additional discussion of the issues with Nigrosin. Given the small difference in wavelength between 405 and 450 nm, it is still reasonable to assess the error in the AAE method of calibrating with Nigrosin. Of the three substances, we demonstrate that Nigrosin has the least reliability for calibration, partially due to this complex relationship between absorption and wavelength. Modifications to the text begin on p7,L29:

“Additionally, the Nigrosin tested here yielded a negative AAE, which is inconsistent with figure 4 of Bluvshstein et al., (2017) in the wavelength range of 400-450 nm that shows a positive AAE. Nigrosin has been shown to have an index of refraction that significantly varies across the visible wavelengths (Bluvshstein et al., 2017), and does not have a relationship between absorption and wavelength that is appropriately modeled by AAE.. However, given that the adjustment is only over a small wavelength range (11% difference in wavelength between 450 nm and 405 nm), the error introduced by adjusting absorption measurements from 450 to 405 nm with the AAE technique is assessed here.”

Comment #15:

P8L17: Use of the Allan deviation is common in the atmospheric community where it is implicitly presented as a detection limit as a function of averaging time. The Allan deviation is useful for identifying drifts, but detection limits and instrument stability are more accurately characterized using the standard deviation which can also be presented as a function of averaging time. I suggest the authors use the standard deviation instead of the Allan deviation.

Response to comment #15: We believe it is important to keep figure 4, the Allan deviation as a function of averaging time, in this paper so as to provide comparison between different instruments and to demonstrate the stability of the instrument. However, based on the comment, we also include a table in the supplement that demonstrates the standard deviation for each cell as a function of averaging time for 1 second, 30 second, and 60 second data. Additionally, the range of standard deviations measured for the four cells is now presented in the main body of the text. Added is Table 1 in the supplement, and the following text, beginning on P8L21:

“As an alternative noise assessment to the Allan deviation, the standard deviation of 1, 30, and 60 second average data are listed for all cells in Table S1 in the supplementary material. The 1 second data standard deviation varies between channels, from 0.01 to 0.12 Mm⁻¹, while at 30 seconds the range is 0.004 to 0.02 Mm⁻¹, and 60 seconds averaging has little change from 30 seconds.”

cell	1 second data (Mm ⁻¹)	30 second average (Mm ⁻¹)	60 second average (Mm ⁻¹)
405 dry	.0092	.0039	.0035
660 dry	.0687	.0321	.0308
405 den	.0250	.0311	.0225
660 den	.1160	.0196	.0199

Comment #16:

P9L10: Please remove one of the periods.

Response to comment #16: corrected

Comment #17:

P9L6: This manuscript should assess the overall measurement accuracy for ambient measurements. This section concludes that the accuracy of these calibrations is roughly +/- 6%. Is this the expected overall accuracy for ambient measurements? If yes, please state that explicitly. If no, please explain why.

Response to comment #17: Yes, this is the expected measurement accuracy based on the calibration. However, the measurement accuracy could also be affected by baseline drifts or abnormally large noise in various situations (aircraft, mobile, etc.). Given this, we only state the accuracy of the calibration, not the accuracy of the actual ambient measurements, which will have to be assessed for every measurement campaign.

Comment #18:

P10L23: please replace '3' with 'three'

Response to comment #18: corrected, thank you

Comment #19:

P11L4: There seem to be a few problems with some of the references. I suggest the authors look over all them carefully. P11L24: Both AMT and AMTD versions of Bluvshstein are in the reference list P12L2: "K??rcher" P12L21: no journal listed P13L19&22: Initials for Lack should capitalized. P13L31: remove "(Julie)" P15L21: No Journal listed

Response to comment #19: thank you for this attention to detail, the full reference list has been worked over and corrected, with the specific problems addressed. The author also found an additional error and made the appropriate fix.

Comment #20:

Figure 1: Could you re-arrange this figure so the flow goes from left to right. Maybe add arrows.

Response to comment #20: Figure 1 has now been re-arranged so that flow goes from left to right, and arrows have been added to show the direction of flow.

Comment #21:

Figure 2: Please change the vertical axis to 'nominal scattering' to indicate it is uncalibrated.

Response to comment #21: The authors thank the referee for this helpful suggestion, and agree that 'nominal scattering' is more correct for this figure, given that the calibration slope has to be applied for true scattering. The title on the vertical axis of figure 2 has been changed.

A novel approach to calibrating a photo-acoustic absorption spectrometer using polydisperse absorbing aerosol

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Abstract. A new technique for calibrating photo-acoustic aerosol absorption spectrometers with multiple laser passes in the acoustic cavity (multi-pass PAS) has been developed utilizing polydisperse, highly-absorbing, aerosol. This is the first calibration technique for multi-pass PAS instruments that utilizes particles instead of reactive gases and does not require knowledge of the exact size or refractive index of the absorbing aerosol. In this new method, highly-absorbing materials are aerosolized into a polydisperse distribution and measured simultaneously with a multi-pass PAS and a cavity attenuated phase shift particulate matter single scattering albedo (CAPS PM_{SSA}, Aerodyne Inc.) instrument. The CAPS PM_{SSA} measures the bulk absorption coefficient through the subtraction of the scattering coefficient from the extinction coefficient. While this approach can have significant errors in ambient aerosol, the accuracy and precision of the CAPS PM_{SSA} are high when the measured aerosol has a low SSA and particles are less than 300 nm in size, in which case where truncation errors are small. To confirm the precision and accuracy of ~~this the~~ new calibration approach, a range of aerosol concentrations were sent to the multi-pass PAS and CAPS PM_{SSA} instruments using three different absorbing substances: Aquadag, Regal Black, and Nigrosin. Six repetitions with each of the three substances produced stable calibrations, with the standard deviation of the ~~measurements calibration slopes~~ being less than 2% at 660 nm and less than 5% at 405 nm for ~~all substances~~ a given calibration substance. Calibrations were also consistent across the different calibration substances (standard deviation of 2% at 660 nm and 10% at 405 nm) except for Nigrosin at 405 nm. The accuracy of the calibration approach is dependent on the single scattering albedo (SSA) of the calibration substance, but is roughly 6% for the calibration substances used here, which all have an SSA near 0.4 at 405 nm. This calibration technique is easily deployed to the field as it involves no toxic or reactive gases and it does not require generation of a monodisperse aerosol. Advantages to this particle-based calibration technique versus techniques based on ozone or nitrogen dioxide absorption include no reactive losses or impact from carrier gases, and the broad absorption characteristics of the particles, which eliminate potentially significant errors in calibration ~~with that would come with~~ small errors in the peak wavelength of the laser light when utilising gas-phase standards.

1 Introduction

_____ Absorbing aerosols represent a significant uncertainty in estimates of global radiative forcing. Black carbon (BC) aerosols, which absorb at all visible wavelengths (Bond et al., 2013) are emitted into the atmosphere as a byproduct of incomplete combustion of biomass and fossil fuels (Bond and Bergstrom, 2006; Jacobson, 2004, 2010). Brown carbon refers to organic aerosol that absorbs much more strongly in the high-energy (blue) portion of the visible spectrum than the red (Bahadur et al., 2012; Barnard et al., 2008; Kirchstetter and Thatcher, 2012; McMeeking et al., 2014). Bond et al. (2013) estimated the global top of the atmosphere radiative forcing of BC to be 1.1 [0.17 –

2.1] W/m², compared to the radiative forcing from CO₂ of +1.68 [1.5 – 1.86] W/m² and CH₄ at +0.97 [0.80 – 1.14] W/m² [2013]. This estimate that BC is the second most radiatively significant emission does not include the radiative effects of brown carbon, which is potentially a significant category of absorbing aerosol, but with larger uncertainty in its optical properties and abundance. Modelling studies indicate that the direct radiative forcing of brown carbon could range up to +0.12 W/m² or +0.57 W/m² (Lin et al., 2014; Saleh et al., 2015). Much of the uncertainty stems from the dependence on mixing state, (Brown et al., 2018; Cappa et al., 2012; Feng et al., 2013; Liu et al., 2015) and from a wide range of reported refractive indices (Chakrabarty et al., 2010; Lack et al., 2012b; Nakayama et al., 2013; Saleh et al., 2013, 2014). The actual radiative forcing of brown carbon is significantly less if it bleaches quickly, but the extent and timeframe of bleaching remain ~~unclear-uncertain~~ (Forrister et al., 2015; Lee et al., 2014; Liu et al., 2016).

Given the significance and uncertainty of absorbing aerosol radiative forcing, it is critical to have accurate and unbiased measurements of aerosol absorption. There are several ways to measure aerosol absorption. Most commonly, absorption is measured by filter-based techniques such as the aethalometer (Hansen et al., 1984), ~~or~~ particle soot absorption photometer (PSAP) (Bond et al., 1999), ~~or~~ continuous light absorption photometer (CLAP) (Ogren et al., 2017) ~~(Ogren et al., 2017)~~. ~~In these approaches,~~ These approaches utilize a measurement of the attenuation of LED laser light energy intensity (typically from an LED) due to absorption by aerosols that are captured on a filter ~~is measured~~, but these techniques are prone to a variety of biases from multiple scattering within the filter itself, variability in backscatter based on the size distribution of the particles, and issues with non-linear responses to loading as the filter becomes saturated (Bond et al., 1999; Collaud Coen et al., 2010; Kondo et al., 2009; Lack et al., 2014; Müller et al., 2011; Weingartner et al., 2003). While filter-based measurements can have high precision, absorption measurements made by filter-based measurements are typically only accurate to within roughly 30-35% (Bond et al., 2013). ~~Ultimately the precision of ambient absorption measurements by filter-based measurements is considered to be roughly 30-35% (Bond et al., 2013)~~. An alternate way to measure absorption is via the difference of extinction and scattering (Wei et al., 2013). The difference method is non-ideal for many types of ambient aerosol due to small measurement errors in extinction and scattering having large impacts on measured absorption levels when the particles are mostly scattering (single scattering albedo is high) (Singh et al., 2014). Scattering measurements are prone to truncation errors for aerosols larger than ~300 nm (when measuring scattering in the visible) due to the high fraction of forward-scattered light for particles with larger size parameters (Onasch et al., 2015).

Photoacoustic spectrometry ~~has~~ emerged as an unbiased and sensitive method for measuring absorption of dry aerosol (Arnott et al., 1999; Lack et al., 2006, 2014; Petzold and Niessner, 1996). ~~The PAS technique is described in detail in the methods section, but a~~ A photo-acoustic aerosol absorption spectrometer (PAS) with a single laser pass can be calibrated based on first principles, if the resonant cell area, resonant frequency, quality factor of resonator, and the laser beam power at the resonant frequency are known (Rosencwaig, 1980). This approach was implemented by Arnott et al. (1999, 2000) and was validated by passing a known concentration of nitrogen dioxide through the instrument. However, the sensitivity of the photoacoustic technique is ~~proportional~~ strongly related to the laser power inside the acoustic cell and increased sensitivity can be achieved through implementation of an acoustic cell where

the laser passes through the cell many times (Lack et al., 2006). Unfortunately, implementation of a multi-pass cell prevents straightforward calibration of the instrument.

~~Theoretically, the absorption coefficient (b_{abs}) can be determined from a PAS as a function of absolute laser power (P_{Laser}), pressure at the microphone (P_{Mic}), resonator cross sectional area (A_{Res}), resonant frequency F_R , and quality factor (Q).~~

$$b_{abs} = \frac{P_{Mic} A_{Res} \pi^2 F_R}{P_{Laser} \gamma - 1 Q} \quad (1)$$

For multi-pass instruments it is difficult (Fischer and Smith, 2018b) or not feasible given the instrument setup (Lack et al., 2012b) to ~~know know all of these terms accurately the absolute laser power within the cavity. This means, meaning~~ the first principles approach of Arnott et al. (1999) is not possible for many instruments. The issue with a fundamental calibration is that the overlap integral of the laser, acoustic mode, and aerosol is not known accurately enough for calibrations. Additionally, the microphone sensitivity and laser power are not known accurately enough for calibration purposes in the design of Lack et al. (2012b). In addition, were this absolute laser power to be determined, the value would change with any small adjustment in alignment. Therefore, another calibration approach must be utilized. Lack et al. (2012b) adopted an approach where ozone enriched air is passed in parallel through a photoacoustic cell and a cavity ringdown cell that is operated at the same wavelength. While this approach has advantages, such as the ease of forming ozone in-situ, there are also significant drawbacks. These drawbacks include 1.) a very small absorption cross section of ozone at 405 nm wavelength ($1.47e-23 \text{ cm}^3 \text{ molecule}^{-1}$ (Axson et al., 2011)) necessitating very high ozone concentrations, 2.) the need to exactly match the laser wavelengths of the PAS and CRDS, 3.) potential reactions or differential wall loss of the ozone between instruments and, 4.) an apparent dependence of the calibration on the bath gas with a nitrogen bath-gas yielding incorrect slopes (Fischer and Smith, 2018a). Even when accounting for these known potential issues with ozone calibration, there ~~remains remain~~ unresolved discrepancies between calibrations performed by different research groups (Bluvshstein et al., 2017; Davies et al., 2018; Fischer and Smith, 2018a). Another option is to calibrate with known concentrations of nitrogen dioxide, instead of ozone, running through both the PAS and CRDS. The primary problem with using NO₂ to calibrate our instrument is ~~While this has the advantage of being able to have calibrated tanks of NO₂, it carries similar negatives to ozone in that NO₂ is toxic and reactive, but additional negatives include that NO₂ photolyzes significantly at an uncertain rate at 405 nm and the magnitude of photolysis depends on the laser power in the instrument~~ (Jones and Bayes, 1973; Lack et al., 2012a), so while it would be a good an excellent calibration standard at 532 nm, it is a poor standard for the two near or below 405 nm cells or our instrument we deem it unfit. Even for 532 nm cells, calibration with NO₂ requires exact matching of laser wavelengths between the PAS and CRDS, has the potential for reactive loss, and requires the use of a toxic substance. While the NO₂ concentrations are often small enough not to pose a significant health hazard, NO₂ use on airborne platforms still requires significant additional safety precautions. Given the issues with gas-phase calibration, it would be desirable to have a particle-based calibration method. In addition to avoiding the issues with reactive gasses, a particle-based calibration would enable detection of particle losses in the

system. Calibration using particles has been attempted by several groups to assess the validity of their PAS calibration (Lack et al., 2006, 2014; Bluvshtein et al., 2017; Fischer and Smith, 2017). All of these groups generated absorbing particles from nigrosin dye and then size-selected ~~the monodisperse~~ aerosols with a differential mobility analyzer (DMA). The aim of this approach is to determine the absorption through Mie theory based on knowledge of the refractive index and size of a monodisperse distribution of spherical particles being sent to the instrument. However, size selection via DMA causes two major issues. First, the concentration of particles is dramatically reduced because only a small fraction of the size distribution passes through the instrument and because uncharged particles are lost. Second, large particles with multiple charges will be passed through the DMA along with the monodisperse particles of interest, which causes significant errors in the calibration because these particles have roughly eight (doubly charged) or more (triply charged) times the mass of the target particles and absorption is roughly proportional to mass. The only way to accurately account for these multiply charged particles is to be confident there are very few particles in the larger size ranges or to add a second DMA ~~to measure the size distribution generated~~. Adding a second DMA is expensive, ~~and adds difficulty to the complexity~~ operationally difficult and ~~may not accurately detect a very even a~~ small number of multiply charged particles ~~will that would cause result in~~ significant ~~error~~error. In addition to the issues of generating a monodisperse distribution, this approach to particle-based calibration ~~also~~ requires exact knowledge of the real and imaginary refractive index of the calibration particles. The refractive index of nigrosin dye has been tested by several groups as an aerosol calibration standard, and three different groups have published estimates of the complex refractive index (RI) of nigrosin at 405 nm (Bluvshtein et al., 2017; Ugelow et al., 2017; Washenfelder et al., 2013). The three studies differ in the retrieved imaginary RI ~~at a given wavelength~~ by 15%, indicating that nigrosin does not have consistent optical properties between different batches and is probably not a ~~good~~ ideal candidate for an ~~absorbing absorption~~ calibration ~~substance~~standard. In fact, there has been a desire for a substance that can be atomized, that absorbs in the visible, and that has a known constant refractive index for several years. Zangmeister and Radney (2018) ~~are currently developing~~have found a substance that can be atomized from aqueous solution that ~~would has a relatively have a~~ constant ~~known~~ refractive index and could eventually be a ~~NIST~~ an aerosol absorption standard, but ~~at this point that this~~ approach still requires selection of a monodisperse ~~aerosol~~ distribution, ~~which has the limitations discussed above~~.

This paper presents a novel calibration technique that utilizes polydisperse absorbing aerosol and does not require a substance with a known refractive index. The technique allows measurement of concentrations spanning from a few Mm^{-1} to several hundred Mm^{-1} , gives consistent results for several different substances across many laboratory calibrations, and has also been used successfully in the field.

2 Materials and Methods

2.1 UW Photoacoustic Absorption Spectrometer

 The photoacoustic absorption spectrometer utilized in this study (referred to from here on as the University of Wyoming PAS or UW PAS) is based on the design of Lack et al. (2012b), with identical cell construction, lasers, mirrors, microphones, speakers and analog signal conditioning. Some important differences are that the Lack et al. PAS has five cells, while the UW PAS has four, two cells operating at ~~a wavelength of~~ 660 nm ~~wavelength~~, and two

at 405 nm. One cell at each wavelength is configured to sample dry air, while the other two are typically plumbed to the outlet of a thermodenuder. For the calibrations presented in this study, the thermodenuded cells are run in a bypass mode and represent a duplicate measurement at each wavelength. The UW PAS has custom data-acquisition software and significantly different vibration isolation and cooling systems than the Lack et al. PAS. While these modifications provide utility and noise suppression, they do not fundamentally alter the operation of the instrument. A brief instrument description follows. Ambient air is pulled through two half-wavelength resonant cells which consist of two cylinders (11 cm in length, 1.9 cm diameter) with quarter-wavelength caps. The primary eigenmode of this instrument consists of one full wavelength across the two cells, such that the antinodes are at the center of each cell and 180 degrees out of phase. ~~The primary eigenmode of this instrument consists of one full wavelength across the two cells, such that the antinodes are at the centre edge of each cell and 180 degrees out of phase.~~ resonates with antinodes at the center of each cell. One cell is illuminated with laser light while the other is not. The signal from the two cells is subtracted in an attempt to remove background noise. Cells are sealed with anti-reflective coated windows to pass laser light, and outside of this enclosed cell are two cylindrical mirrors rotated 90° out of phase. The front mirror has a 2 mm hole to pass a collimated laser beam, and radius of curvature of 430 mm, while the back mirror cylindrical radius is 470 mm. The mirrors are treated with a dielectric coating to be 99.5% reflective. When appropriately aligned, the end result is an astigmatic pattern that produces many (theoretically 182) passes of the laser light, with energy lost from scattering off the mirrors and windows at each pass and several potential versions of the astigmatic pattern, each with different numbers of passes. The light loss depends on how clean the system is as well as system alignment and ~~is the~~for this reason quantification of laser power in the cell is ~~nearly impossible~~not possible without a significant amount of additional ~~instrumentation~~equipment. The laser power is modulated at the resonant frequency of the cell and interacts with absorbing ~~components of the~~ aerosol in the cell, which heat and expand the air around them at the frequency of modulation. The resulting acoustic wave is measured by two microphones (Knowles Corp. EK-23132-000) placed at each antinode (one in the cell with laser light passing through it and one in the dark cell). The subtraction and amplification of the two microphone signals is done on a signal processing board identical to that described in Lack et al. (2012b). ~~The analog signal,~~ is then digitized, ~~and then undergoes~~converted via a Fourier transform into frequency space. The power at the peak resonant frequency is summed with the power 1 Hz to either side of the peak, so that the total signal ~~retained~~is an integrated area across three points, each 1 Hz apart. Thus, the signal from each PAS cell is referred to as integrated area (IA).

~~The~~To obtain the maximum, and consistent, signal the ~~laser lasers~~ must be modulated at each cell's resonant frequency, which is dependent on temperature and pressure in the cell. Accordingly, ~~so~~ a resonant frequency calibration is performed at a regular intervalintervals (typically at least every 5 minutes) ~~whatever interval~~, to account for any drifts in temperature or pressure ~~(typically at least every 5 minutes)~~. There is a speaker (Knowles Corp. EP-24075-000) in each cell for this purpose, ~~and a speaker calibration is performed regularly to determine the resonant frequency.~~This resonant frequency calibration is ~~currently~~performed in a different way than Lack et al. (~~2012b~~). The speaker output is swept over range of ~~resonant~~frequencies at constant output power and the frequency that gives the maximum integrated area is found. The first calibration is done over a wide range of frequencies (1640-1370 Hz),

then subsequent calibrations are done over ~5 Hz ranges given that the resonant frequency has never been observed to vary by more than this between frequency calibrations.

2.2 CAPS PM_{SSA}

~~The Aerodyne's Aerodyne~~ CAPS PM_{SSA} instrument combines a cavity attenuated phase shift (CAPS) measurement of extinction with an integrating nephelometer measurement of scattering. The instrument uses a form of cavity-enhanced spectroscopy by which a square wave modulated light emission from an LED is detected as a phase-shifted signal, ~~that can be converted to from which~~ extinction ~~can be calculated~~ (Kebabian et al., 2007). At the same time, scattered light from particles in the CAPS cavity is integrated across all angles minus the extreme forward and backward directions. The details of the CAPS PM_{SSA} design, principles of operation, calibration, sensitivity, and measurement uncertainty are presented in Onasch et al. (2015). The advantage of a single instrument that can measure the single scattering albedo of bulk aerosols in real time is that it minimizes potential sampling ~~errors issues and that can cause biases error~~ between the scattering and extinction measurement. The extinction measurement is absolute (similar to cavity ringdown spectroscopy) and therefore does not require routine calibration. The scattering channel is calibrated by linking it to the extinction measurement through measurements of a purely scattering aerosol, as discussed in Section 3.1. The main difficulty with using a CAPS PM_{SSA} to measure the scattering coefficient of ambient aerosols is the truncation of light scattered from larger particles that tend to have a phase function where a large fraction of light is scattered in the forward direction. Onasch et al. (2015) calculated the truncation as a function of PSL diameter for 660 nm and 450 nm wavelength instruments, and demonstrated that the truncation only becomes significant for particles larger than 300 nm in diameter.

2.3 Generation of absorbing aerosol for PAS calibration

Three different absorbing substances were used in this study: Aquadag, Nigrosin, and Regal Black. All three are commonly used to generate absorbing aerosol for optical measurements ~~by photoacoustic absorption spectrometers, and Aquadag is commonly used or for measurements by calibration of~~ the single particle soot photometer (SP2) (Baumgardner et al., 2012; Gysel et al., 2011; Jordan et al., 2015; McMeeking et al., 2014; Saleh et al., 2013). Aquadag (Lot#ON03616890) is a high-viscosity slurry while Nigrosin (Lot#BCBR0628V) and Regal Black (Batch#400R GP-3901) are solid crystals. For all three substances, the method of generating a solution was the same. The exact concentration of the solution is not critical because atomized particles ~~will beare~~ diluted with particle-free air, but the size distribution is important due to the need to have particles smaller than 300 nm to limit truncation in the scattering channel of the CAPS PM_{SSA}. ~~A small amount, a~~ few crystals (solids) or a quarter spatula (slurry), of the given substance is mixed with Milli-Q water (Millipore system SimPak2) and progressively diluted ~~(starting with a couple hundred ml of water)~~ until the size distribution of the atomized aerosols ~~has is such that~~ 99% of the mass ~~is~~ below 300 nm. ~~More dilute solutions tend to yield aerosol with smaller sizes.~~ After generating a reasonable solution that has a peak in its number size distribution from 40-70 nm, the solutions are sonicated for 15 minutes to ensure they are completely dissolved or well mixed with the water.

Figure 1 shows a schematic of the experimental setup. Absorbing aerosols are generated from ~~the solutions~~ solution using a constant output atomizer (TSI) fed with particle-free (pulled through a HEPA filter) air at 20 psi. The aerosol is then passed through a silica gel diffusion drier (TSI) and further diluted with particle-free air to achieve the desired ~~dilution~~ concentration. The dilution is varied so that a range of concentrations can be measured. The aerosols are dried a second time with a ~~nafion~~ Nafion tube drier (PurmaPure PD-100T) that is a permanent part of the UW PAS inlet before the flow is split to four different instruments – the 4-cell PAS, two different wavelength (450 nm, 660 nm) CAPS PM_{SSA} instruments and a TSI scanning mobility particle analyser (SMPS), which is a combination of a differential mobility analyser (DMA) and condensation particle counter (CPC). The SMPS is set up with a 10:1 ratio of sheath to sample flow, using flow rates of 3 liters per minute (lpm) for ~~the~~ sheath and 0.3 lpm ~~for~~ ~~the~~ sample. The output from the DMA is diluted with 0.7 lpm of filtered air to achieve a 1 lpm flowrate for the CPC.

3 Results and Discussion

~~_____~~ The ~~overall idea~~ concept of the calibration method is to calibrate a multi-pass PAS based on the absorption of small, highly absorbing ($SSA < 0.5$), particles ~~for which the absorption can be accurately~~ measured by the CAPS PM_{SSA}. To ensure accurate results, the performance, accuracy and precision of the CAPS PM_{SSA} measurement of absorption, through ~~the difference of~~ extinction ~~minus and~~ scattering, must first be verified.

3.1 Calibration of the CAPS PM_{SSA} scattering channel

~~_____~~ The scattering channel for the CAPS PM_{SSA} is calibrated relative to the extinction channel, because the extinction does not require calibration ([Onasch et al., 2015](#)). To calibrate the scattering channel, polydisperse ammonium sulfate was atomized, dried, and diluted following the methods described in section 2.3. The mean geometric diameter of the atomized solution was tuned (through dilution of the atomized liquid) to be close to 55 nm, with less than 1% of the mass at diameters greater than 300 nm, as verified by the SMPS. The concentration of the purely scattering ammonium sulfate aerosol is varied to achieve extinction coefficient values ranging from $\sim 5 \text{ Mm}^{-1}$ to $\sim 600 \text{ Mm}^{-1}$. A linear fit to the resulting data gives the relationship between the scattering coefficient and extinction coefficient derived by a particular instrument. Figure 2 shows an example of one calibration. The intercept in all cases is very close to zero, and is not used because baseline corrections with a filter are made at regular intervals automatically by both instruments. In Fig. 2a the 660 nm instrument has a ratio of scattering to extinction of 0.9045, so the true scattering coefficient is the reported scattering coefficient divided by this slope. Similarly, in Fig. 2b, the scattering signal must be divided by 1.0423. Across 6 calibrations done in this manner, the 450 nm CAPS PM_{SSA} calibration slope was 1.0439 ± 0.0073 (0.7% standard deviation ~~from of~~ the mean). For the 660 nm instrument, the ratio of scattering to extinction averaged over 6 calibrations is 0.890 ± 0.018 (2% standard deviation from the mean). The errors in this calibration are included in the error estimate for the accuracy of this calibration technique.

Tests were ~~also~~ performed to ~~confirm~~ ~~verify~~ the accuracy of the extinction measurement in the CAPS PM_{SSA}. In these tests PSL of various sizes were ~~sent to the size selected by a~~ SMPS then the flow from the SMPS was split between a TSI 3010 CPC and the CAPS PM_{SSA}. It was found that the extinction measured by the CAPS PM_{SSA} was within 5% of the extinction calculated based on Mie ~~calculations~~ theory using the PSL size and the number of

particles measured by the CPC. The error between the Mie calculations and the CAPS PM_{SSA} is within what is expected based on the size range stated for the PSL's, the counting accuracy of the CPC, and the stated accuracy of the CAPS PM_{SSA}.

3.2 Calculation of AAE for each substance

The UW PAS has two cells that operate at a wavelength of 405 nm and two that operate at a wavelength of 660 nm. While the red-LED CAPS PM_{SSA} instrument also operates at 660 nm, the blue-LED CAPS PM_{SSA} operates at 450 nm, a mismatch with the PAS wavelength. Initially a 405 nm CAPS PM_{SSA} instrument was built, but the 405 nm mirrors rapidly degraded requiring ~~going back a return~~ to the 450 nm wavelength. We demonstrate here that accurate calibration with the proposed method is feasible even when the instruments are ~50 nm separated in wavelength. This suggests that one could calibrate PAS instruments at different wavelengths without having to have a CAPS PM_{SSA} instrument to exactly match every PAS wavelength. Currently CAPS-PM_{SSA} are available at 630, 660, 530, and 450 nm.

To account for the wavelength difference between the CAPS PM_{SSA} (450 nm) and the UW PAS (405 nm), the absorption angstrom exponent (AAE) was calculated based on the 660 nm and 450 nm CAPS PM_{SSA} measurements of absorption for each calibration and substance. This calculated AAE can then be used to convert the 450 nm absorption coefficient measured by the CAPS PM_{SSA} into an estimate of the 405 nm absorption coefficient needed to calibrate the multi-pass PAS. Equation (42) shows how AAE is calculated from the two different wavelength CAPS PM_{SSA} measurements of absorption coefficient, and the same relationship is used to convert absorption at 450 nm to absorption at 405 nm.

$$AAE = -\frac{\log\left(\frac{b_{abs,660}}{b_{abs,450}}\right)}{\log\left(\frac{660}{450}\right)} \quad (42)$$

The ~~experimental~~ experimentally derived AAE is different for each of the three substances used in this study allowing for an assessment of the accuracy of utilizing AAE derived from measurements at 660 and 450 nm to convert from absorption at 450 nm to absorption at 405 nm. Six different calibrations were conducted with each substance to assess the stability of the estimated AAE. For Aquadag, the average AAE (+/- 1σ) was 0.3423 +/- 0.0357, for Regal Black it was 1.053 +/- 0.022 and for Nigrosin it was -0.4687 +/- 0.1127. The standard deviation expressed as a percentage for each of the substances is: 2% for Regal Black, 10% for Aquadag, and 24% for Nigrosin. These results suggest that, of these substances, Regal Black may be the best choice for this calibration technique because it has a very stable AAE and the AAE is close to 1, which is often the assumption made for black carbon (Bergstrom et al., 2002; Lack et al., 2012b; Moosmüller et al., 2009, 2011). Aquadag is also a good choice because, while it has slightly more variability in its AAE, the AAE itself is smaller than that of Regal Black meaning the accuracy of its value is mathematically less critical. Nigrosin had a ~~much~~-higher standard deviation than either Regal Black or Aquadag, perhaps suggesting that even within a single batch the substance does not have consistent optical properties. Additionally, the Nigrosin tested here yielded a negative AAE, which is inconsistent with figure 4 of Bluvshstein et al. (2017) in the wavelength range of 400-450 nm that shows a positive AAE, ~~who found a slightly positive AAE, a~~

result that is discussed further in Section 3.6. The standard deviation expressed as a percentage for each of the substances is: 2% for Regal Black, 10% for Aquadag, and 24% for Nigrosin. These results suggest that, of these substances, Regal Black may be the best choice for this calibration technique because it has a very stable AAE and the AAE is close to 1, which is often the assumption made for black carbon (Bergstrom et al., 2002; Lack et al., 2012b; Moosmüller et al., 2009, 2011). Aquadag is also a good choice because, while it has slightly more variability in its AAE, the AAE itself is smaller than that of Regal Black meaning the accuracy of its value is less critical. Nigrosin has been shown to have an index of refraction that varies across the visible wavelengths (Bluvshstein et al., 2017), and does not have a relationship between absorption and wavelength that is perfectly modeled by AAE. However, given that the adjustment is only over a small wavelength range, the error introduced by adjusting absorption measurements from 450 to 405 nm with the AAE technique is Nigrosin has been shown to have an index of refraction that significantly varies across the visible wavelengths (Bluvshstein et al., 2017), making the utilization of AAE for Nigrosin potentially less robust. The error introduced by adjusting absorption measurements from 450 to 405 nm with measured AAE was also assessed still assessed here. Nigrosin has the largest variation in calculated AAE from the different calibrations, but the difference in absorption at 405nm calculated from the highest AAE (-0.3) to the lowest (-0.6), a factor of two in AAE, is only 3%. This demonstrates that even with significant variation in AAE the calibration method is still robust and this adjustment in wavelength causes minimal error. The errors introduced by AAE for Regal Black and Aquadag are significantly smaller than that for Nigrosin. Figure 3 shows 1 Hertz data from one of the six calibrations with each substance. The AAE for a given substance is fairly stable but does grow noisy when absorption values are $<10 \text{ Mm}^{-1}$. This noise is particularly pronounced in panel (c), when small ($\sim 5 \text{ Mm}^{-1}$ absorption) concentrations of Nigrosin do not produce a stable enough signal in the two CAPS PM_{SSA} instruments to accurately calculate AAE.

3.3 UW PAS stability

Before applying the CAPS PM_{SSA} calibration to the UW PAS, the noise level of the UW PAS was assessed by plotting the Allan deviation as a function of time. A similar analysis for the CAPS PM_{SSA} can be found in Onasch et al. (2015). The Allan deviation as a function of averaging time is displayed for each cell in the instrument in Fig. 4. While the behavior of each cell is slightly different, on average across the four cells of the instrument, the 1 second Allan variance is 0.6 Mm^{-1} and it is 0.5 Mm^{-1} for the best performing cell. After 60 seconds of averaging, the noise drops nearly an order of magnitude to 0.09 Mm^{-1} on average and 0.06 Mm^{-1} in the lowest noise cell. As an alternative noise assessment to the Allan deviation, the standard deviation of the mean is also noted for each cell at 1 second data, 30 second average, and 60 second average data. The values for each cell are listed for all cells in Table S1 in the supplementary material. The 1 second data standard deviation of the mean varies significantly between channels, from 0.00921 to $0.116.12 \text{ Mm}^{-1}$, while at 30 seconds the range is 0.003874 to 0.01962 Mm^{-1} , and 60 seconds averaging has little change from 30 seconds, with a range of 0.00354 to 0.0199 Mm^{-1} .

3.4 Precision of calibration results

As described in section 2.3, Nigrosin, Aquadag, and Regal Black were aerosolized and passed to the 4 PAS cells (two 405 nm cells, two 660 nm cells), 2 CAPS PM_{SSA} cells (660 and 450 nm), and an SMPS. The purpose of measuring with an SMPS was to confirm that only a negligible fraction of the polydisperse aerosol mass was at diameters > 300 nm. Aerosol size distributions for each substance are displayed in Fig. S1. Absorption was determined at 450 nm and 660 nm by subtracting the CAPS PM_{SSA} measurement of scattering from CAPS PM_{SSA} measurements of extinction. The absorption at 405 nm, where the PAS operates, was determined via measurements of the AAE as outlined in section 3.3. The resulting calibration slopes for each channel across 6 calibrations are shown in Fig. 5 and Table 1. The standard deviation of the 6 different calibration slopes at 660 nm have a maximum standard deviation of 1.2% of the mean (~~for~~ Regal Black has this largest standard deviation). At 405 nm, the variation is larger, with Nigrosin having the largest standard deviation between the calibrations of ~~the mean at~~ 4%. In practice, the calibration slopes are applied to the PAS microphone signal to convert from integrated area to absorption (as outlined in section 2.1). A filter/filter period/periods are frequently conducted to determine the background absorption and the PAS data is zeroed to this background. Large (on the order of several hundred Mm⁻¹) concentrations are used to generate a slope that can be applied over significant concentrations in field measurements of smoke particles. Therefore, intercepts can be on the order of 10 Mm⁻¹. The intercepts from the calibration slope determination process/calibrations are not used.

Variations over the six calibrations using a single substance are quite small and for the 660 nm data variation between the substances is also small (~~4XX %~~). However, there is more variation between the three different substances in the blue, up to a ~~1720%~~ difference between Nigrosin and Aquadag, though the results for Aquadag and Regal Black are within 5% of one another. We hypothesize that the optical properties of Nigrosin may vary in such a way that assuming an AAE between 450 nm and 405 nm may be inappropriate.

3.5 Accuracy of calibration

_____ The previous section demonstrated that the precision of the calibration method ~~is~~ is fairly precise with less than 5%, based on the variation in the average of six calibration runs or between the results from different substances (other than Nigrosin at 405 nm, which appears to be an outlier). Next, the accuracy of the method is assessed. The fractional accuracy of the extinction coefficient measured by the CAPS PM_{SSA} is found by Onasch et al. (2015) to be ± 0.05 or 5%. The fractional error in SSA is reported by Onasch et al. (2015) to be 0.01 or 1%, but we find that it is slightly larger for our instrumental setup at 0.02 or 2%. We derive this slightly larger error in SSA ~~because this was from~~ the variability in our six repetitions of the scattering to extinction calibration for the CAPS PM_{SSA}. ~~The One way to find the~~ absorption coefficient ~~can be found~~ from CAPS PM_{SSA} data is via equation-Equation (23)

$$\text{Absorption} = \text{Extinction} * (1 - \text{SSA})$$

(23)

We utilize this equation because it allows the error to be couched in terms of SSA. Given this, the fractional error in the absorption coefficient, defined here to be σ_{abs} , is found by adding the fractional errors in extinction and the fractional error in the term (1-SSA) in quadrature. This can only be done if the errors are independent. In this case independence is a reasonable assumption because the error in extinction is caused by the accuracy of interpreting the phase-shifted signal in the CAPS while the error in SSA is caused by the ability to match the scattering signal to the extinction signal, as discussed in section 3.1. Given this, the error in the extinction does not depend on the error in the SSA and vice versa. The error in the term (1-SSA) is simply two percent of the SSA because the integer 1 has no error. This yields an equation for the fractional error in the absorption coefficient of

$$\sigma_{abs} = \sqrt{\sigma_{ext}^2 + \left(\frac{0.02*SSA}{1-SSA}\right)^2}$$

(43)

where σ_{abs} is the fractional error in absorption and σ_{ext} is the fractional error in extinction. ~~This~~ The fractional error in absorption (σ_{abs}) is displayed (as a percent) as a function of SSA in Fig. 6. As SSA goes to 0, the error in absorption approaches the 5% limit which is the error in extinction alone, but as SSA approaches 1 the error goes to infinity. The SSA of the three calibration substances in the current study are all close to 0.4, which yields an error of approximately $\pm 5.2\%$. The high error above an SSA of ~ 0.85 is a good indicator of the limits of using the CAPS PM_{SSA} for measuring absorption in ambient conditions, and one of the main motivations for making absorption measurements with the PAS measurements instrument. ~~This Figure 6 graph~~ also gives guidance into the highest SSA substances that one might consider using to calibrate a multi-pass PAS with the CAPS PM_{SSA}, based on the level of accuracy desired. Finally, at very low levels of absorption-extinction, the errors are not defined by equation-Eq.uation (34), but but are rather dominated by the detection limits of the CAPS PM_{SSA}. Despite this, equation-Eq.uation (34) is a good representation of the calibration error for the technique presented here because the slope of the calibration line is controlled by measurements with sufficient absorption-extinction that equation-(3) is valid (see Fig. 5).

3.6 Mie theory applied to the Nigrosin calibration

The refractive index of Nigrosin dye was derived by Bluvshstein et al. (2017) through ellipsometry at both 405nm (m=1.624 + 0.154i) and 660nm (m=1.812 + 0.246i). ~~To evaluate the accuracy of the current calibration approach in another way other than the error propagation done in the previous section, the~~ The theoretical absorption of the polydisperse Nigrosin particles used during the-the calibration-calibrations done in this paper was calculated from Mie theory assuming these refractive indices and compared to the absorption measured by the CAPS PM_{SSA}. Size distributions were measured by the SMPS, and absorption estimates were made for every SMPS scan yielding 3 independent calculations of absorption for every concentration level. We also performed this calculation at multiple tested for other indices of refraction that have been previously published in the literature. Figure 6a-7a shows CAPS absorption measured versus calculated absorption from Mie theory at 660 nm using the RI derived by Bluvshstein et al. (2017) (m=1.812 + 0.246i) and demonstrates excellent-good agreement. The same calculations were done at 405nm and 450 nm using the Bluvshstein et al. (2017) values (m=1.624 + 0.154i at 405nm, m=1.605 + 0.190898i at

450nm), but in this case the ratio of measured CAPS absorption to calculated absorption from Mie theory is ~ 0.58 for both the 405 nm comparison and the 450 nm comparison. The RI ~~for~~ that gives the best agreement between the 450 nm CAPS PM_{SSA} measured absorption and Mie theory, shown in Fig. ~~6b7b~~, is $m = 1.600 + 0.105i$. This refractive index is similar to the result ~~by-given in~~ Liu et al. (2013) of $m = 1.61 + 0.12i$. The discrepancy between the current result and that from Bluvshstein et al. (2017) and different refractive indices found in the literature at 405 nm for Nigrosin ((Washenfelter et al. 2015) $m=1.66 + 0.183i$; (Ugelow et al., 2017) $m=1.57 + 0.133i$) suggest that different batches of Nigrosin have significantly-different absorptivity and that Nigrosin may not be a good calibration substance at shorter visible wavelengths.

4. Conclusions

_____A new calibration method for multi-pass photoacoustic absorption spectrometers that uses polydisperse absorbing aerosol and an accompanying measurement of absorption from the CAPS PM_{SSA} instrument has been presented. This method is demonstrated to be consistent over repeated trials and across three different aerosol types, namely Aquadag, Regal Black, and Nigrosin. The calibration curve represents the relationship between absorption as measured by the CAPS PM_{SSA} to integrated area as measured by the PAS ~~microphones~~, and is demonstrated to be linear and spanning over three orders of magnitude in absorption, up to $\sim 600 \text{ Mm}^{-1}$ ~~of absorption~~. The method is found to have an absolute accuracy of less than approximately $\pm 6\%$ for the substances tested. This aerosol-based method of calibration is simple and easy to utilize in both the laboratory and the field, and does not require size-selection. By using absorbing particles, we eliminate several potential concerns from gas-phase calibrations using nitrogen dioxide or ozone. Namely, there is no potential for reactive losses and concentrations on the order of 100^3 of Mm^{-1} are easily and safely attained. Additionally, small differences in wavelength between instruments are of negligible consequence. To accommodate for a wavelength difference between 405 nm PAS cells and the 450 nm CAPS PM_{SSA} , we calculate the AAE of each species based on the relationship between 660 nm and 450 nm measured absorption coefficients from the CAPS PM_{SSA} and apply this to convert the 450 nm absorption coefficient to the absorption coefficient at 405 nm. This is also shown to have small uncertainties, $<3\%$. We also Finally, we derive the refractive index of a particular batch of Nigrosin at 450 nm to be $m = 1.600 + 0.105i$, and confirm a previous result at 660 nm of $m = 1.812 + 0.246i$.

Data availability. All data are available from the corresponding authors upon request.

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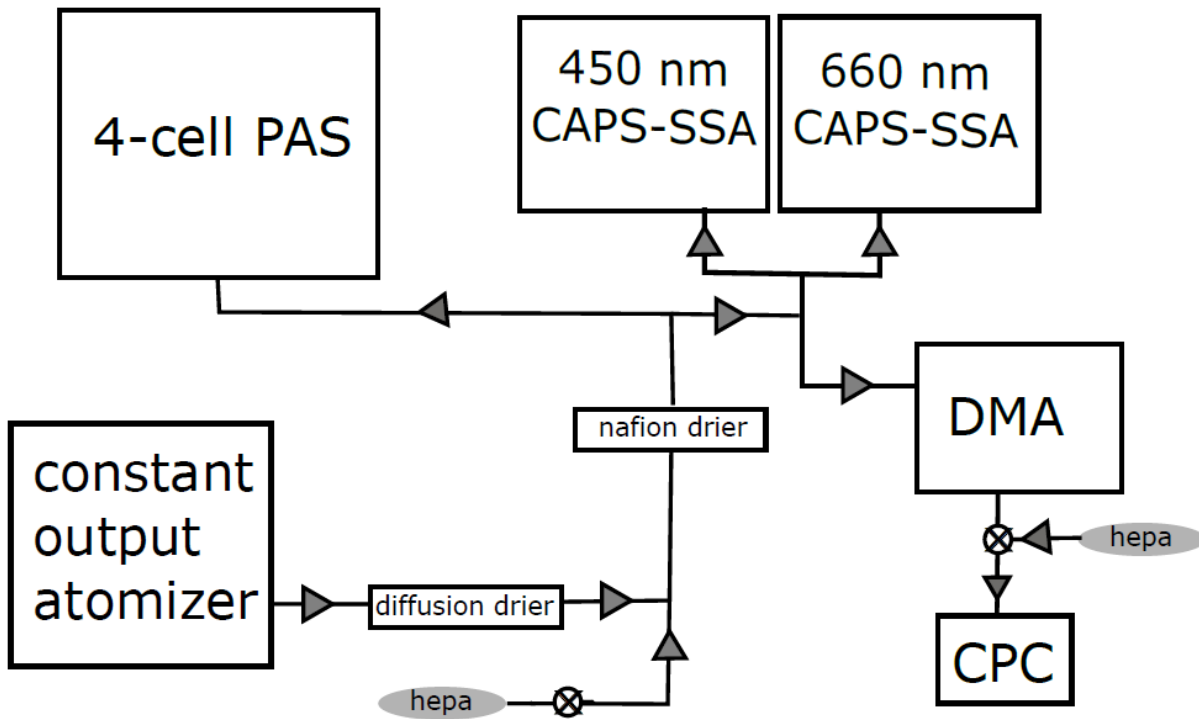


Figure 1: Schematic of the calibration setup. Flow begins in ~~bottom~~ the bottom left right at the constant output atomizer, then the aerosols are diluted and dried before being distributed to each instrument. The DMA is a TSI's-TSI differential mobility analyzer, and the CPC is ~~the a TSI 3010~~ a TSI 3010 condensation particle counter. When combined, these two instruments are referred to as a scanning mobility particle sizer.

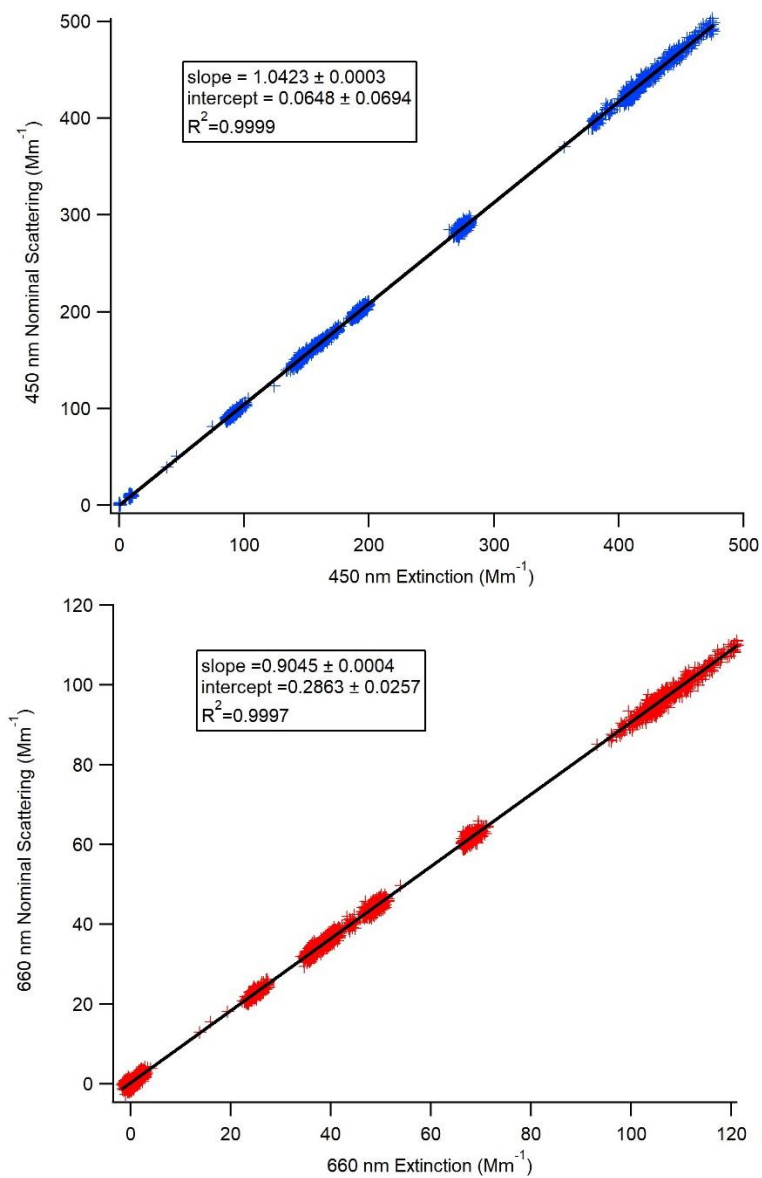


Figure 2: Calibration-Scattering calibration curves for each of the Aerodyne CAPS PM_{SSA} instruments. The scattering channel is calibrated based on the relationship to the extinction channel across a range of concentrations. The slope of the resulting linear fit gives the ratio that scattering must be corrected by.

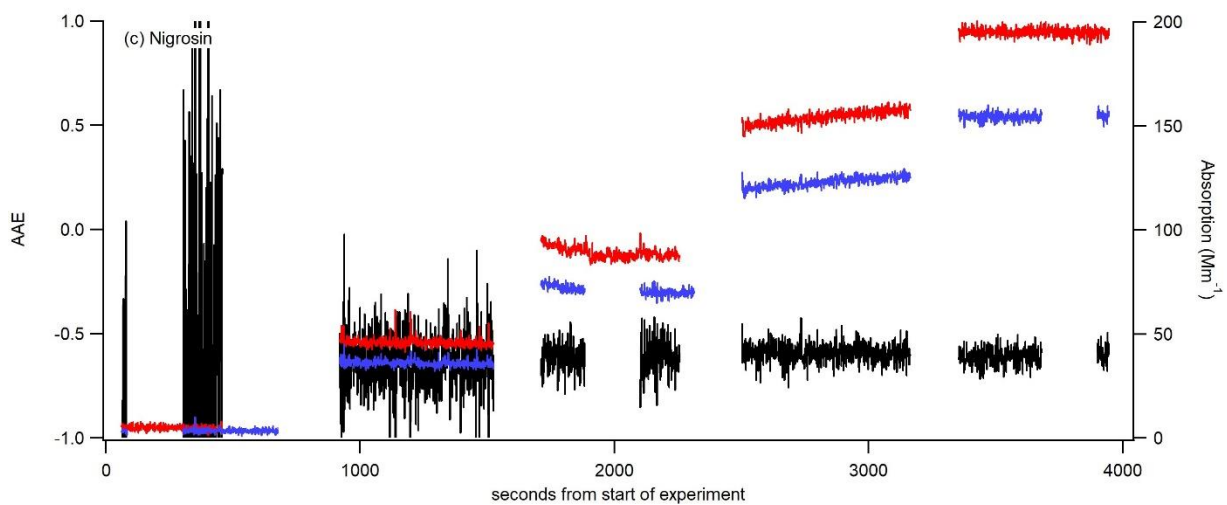
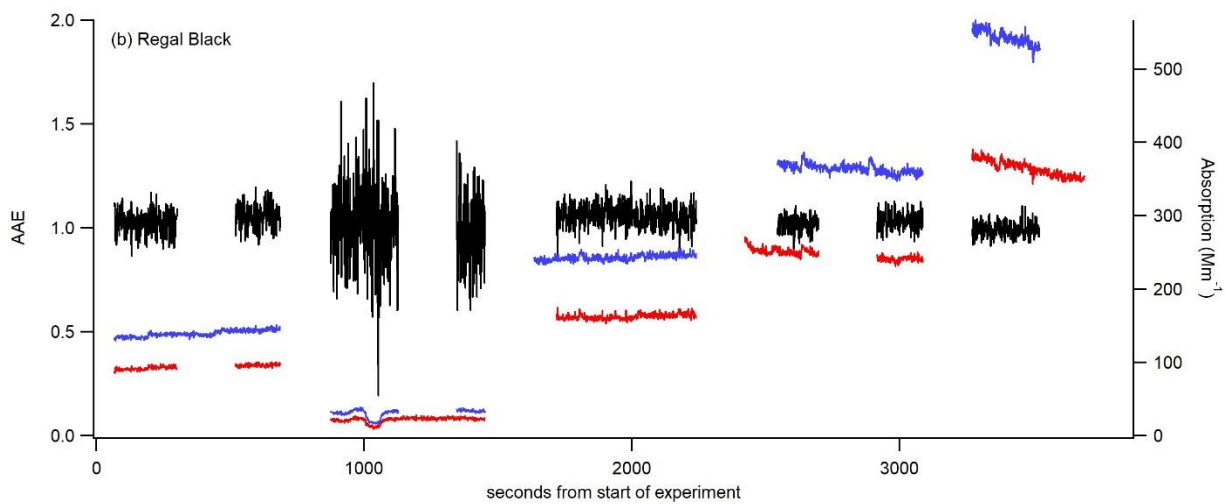
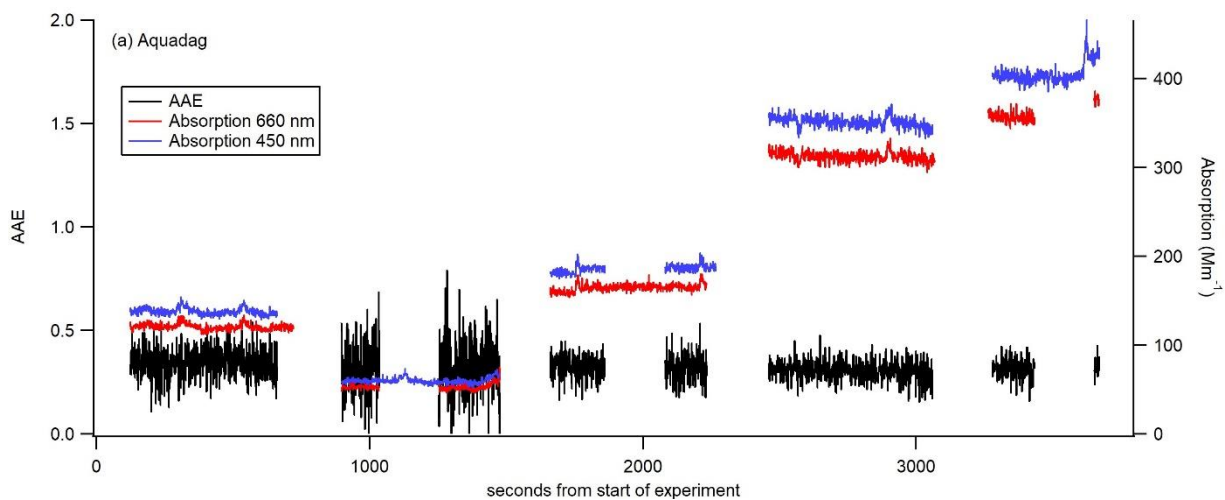


Figure 3: AAE (black) calculated from 1 Hertz data from the CAPS PM_{SSA} data for three different substances: Aquadag (3a), Regal Black (3b) and Nigrosin (3c). Also shown are 660 nm extinction (black) and 660 nm absorption (red) coefficients taken from the CAPS PM_{SSA} instrument. The extinction and absorption coefficients are shown for context, as the AAE becomes significantly more noisy at low concentrations. Gaps in data occur when the CAPS is conducting a baseline period, and the instruments are switched to filter for several minutes in between each concentration.

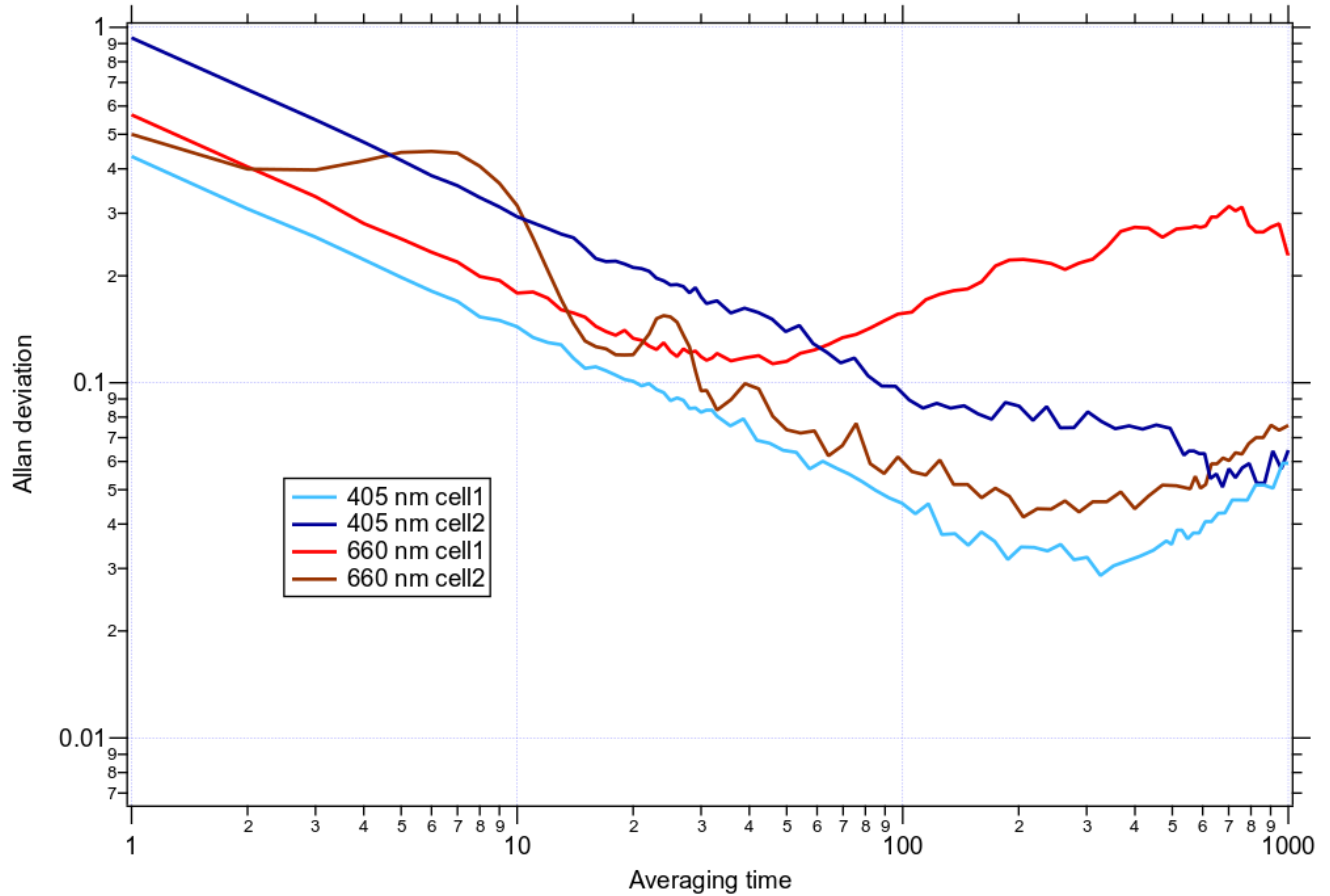


Figure 4: Allan deviation versus averaging time for the UW PAS during filter period measuring filtered air. The PAS has 4 cells- 2 at 660nm and 2 and 405nm. During operation one cell at each wavelength can pull denuded air while the other pair of cells measures absorption of dry air.

Substance	Average AAE	Average slope at 660nm (Mm ⁻¹ /Arb Unit)	Average slope at 405nm (Mm ⁻¹ /Arb Unit)
Regal Black	1.053 ± 0.021	944 ± 12	2270 ± 65
Aquadag	0.342 ± 0.036	961 ± 11	2390 ± 33
Nigrosin	-0.469 ± 0.112	921 ± 10	1980 ± 75

Table 1: Summary of AAE and clibration slopes for each substance, reported as average and standard deviation from six calibrations.

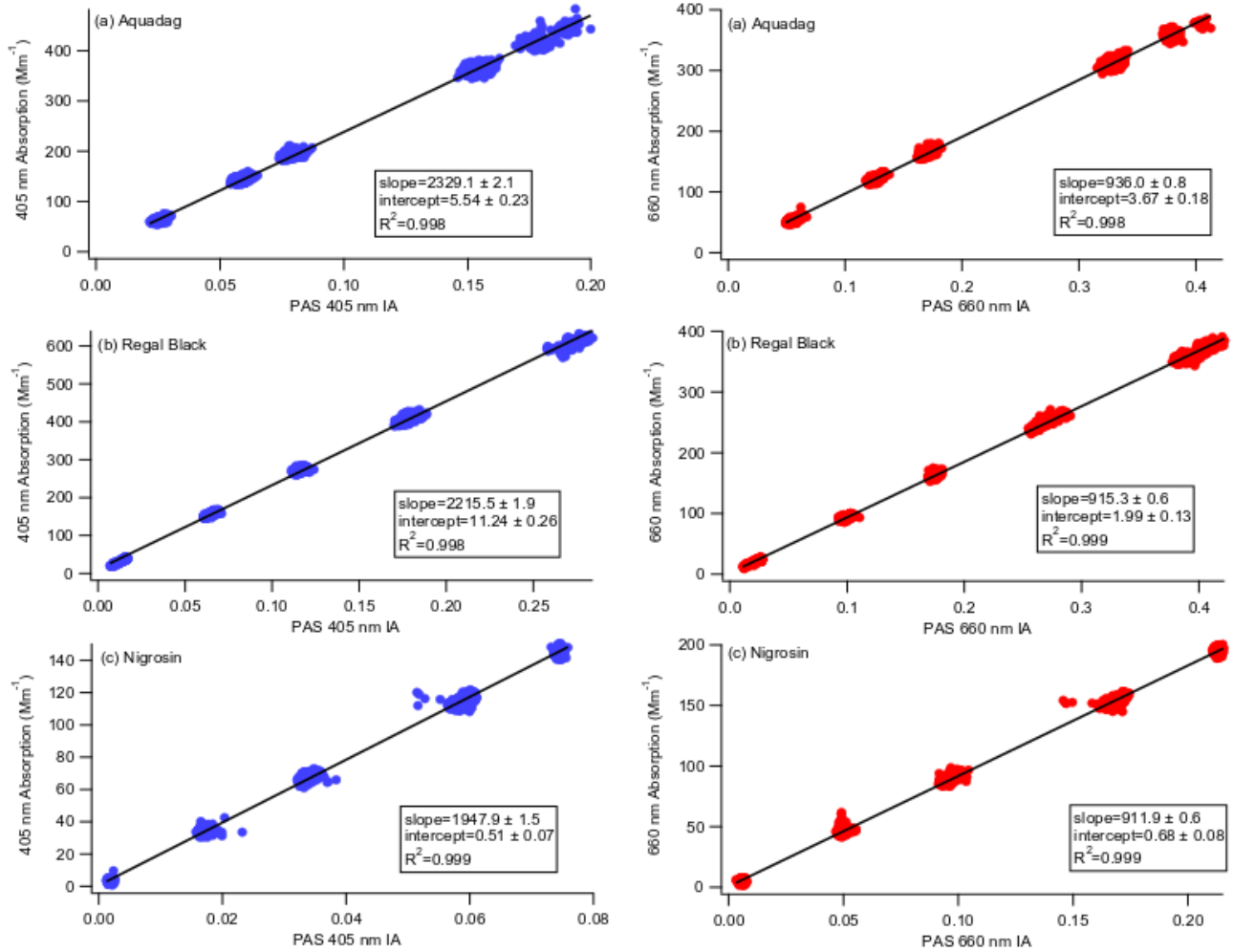


Figure 5: Calibration curves representing CAPS PM_{SSA} absorption versus PAS Integrated Area (IA). The PAS 405 ~~dry~~ nm cell is on the left, 660 ~~dry~~ nm cell on the right. A line is fit to the data, the slope of which gives the relationship between absorption and IA. Intercepts are allowed to vary in order to achieve the most accurate slopes based on higher absorption levels where the accuracy of the CAPS PM_{SSA} is highest. During operation in the field, both instruments are frequently zeroed based on filter measurements, meaning the intercept of the calibration slope is not needed.

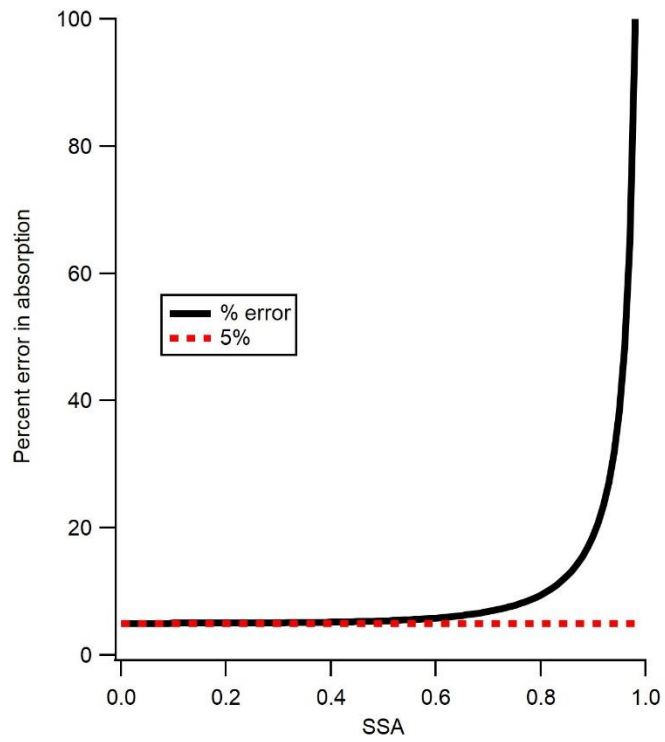


Figure 6: Percent error in absorption versus single scattering albedo (SSA), following Eq. (34). As SSA approaches zero, absorption error approaches 5%, as SSA approaches 1, the error goes to infinity. ~~An SSA of 0.98 has 100% error in absorption.~~

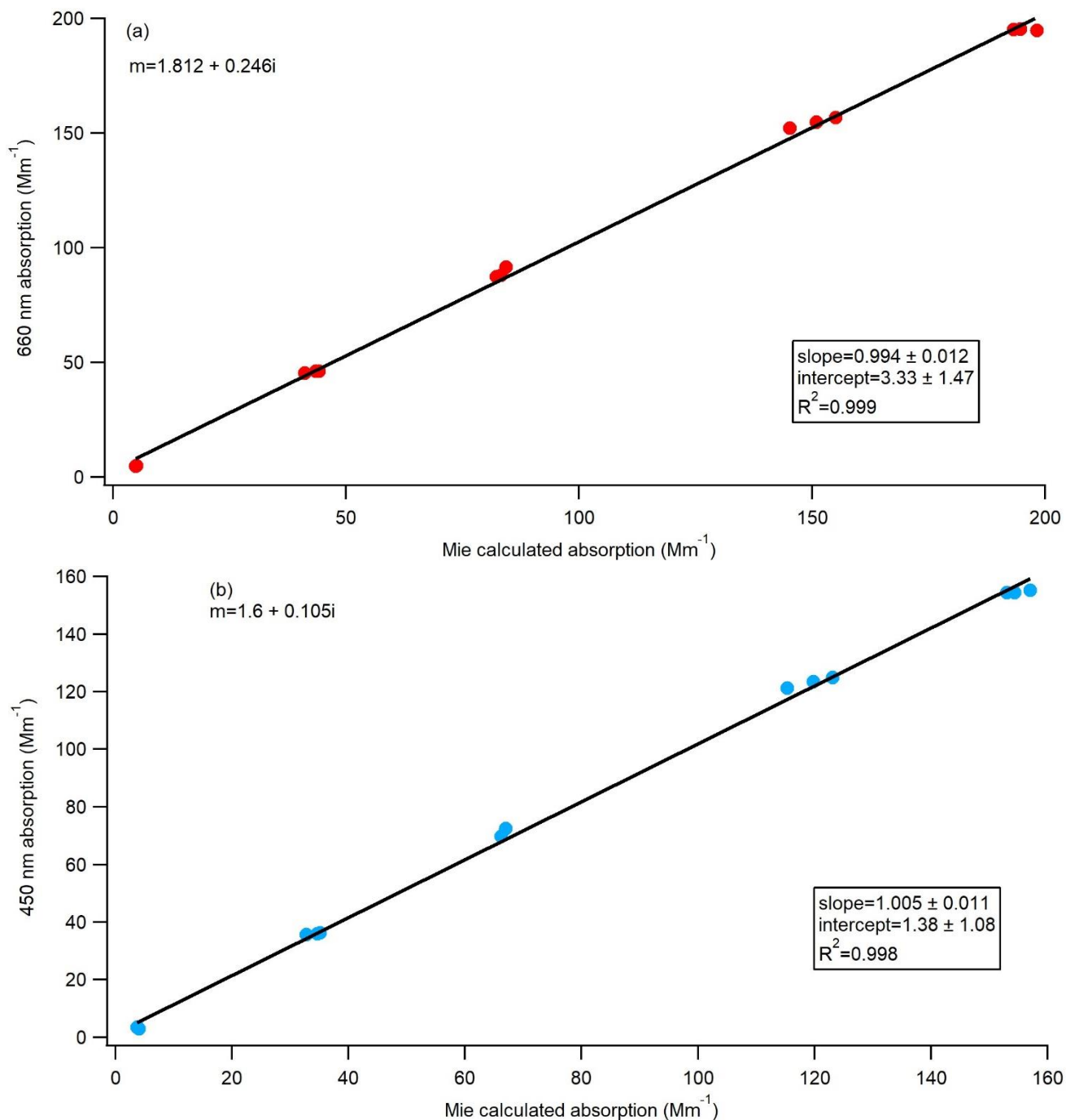


Figure 7: Absorption from CAPS PM_{SSA} data versus calculated absorption from SMPS size distributions, using Mie theory and the refractive indices as shown in figure. Panel (a) is ~~from~~ for the 660 nm instrument, ~~with calculated absorption using the RI as in Bluvshstein et al. (2017),~~ while panel (b) is from the 450 nm instrument compared to our calculated RI.

Table S1: Noise levels of the PAS taken during filter period. Reported is the standard deviation of the mean as a function of averaging time for each of the four PAS cells.

cell	1 second data (Mm^{-1})	30 second average (Mm^{-1})	60 second average (Mm^{-1})
405 dry	.0092	.0039	.0035
660 dry	.0687	.0321	.0308
405 den	.0250	.0311	.0225
660 den	.1160	.0196	.0199

Figure S1: Aerosol size distributions from the three different substances used for the calibration method: Aquadag (a), Regal Black (b), and Nigrosin (c). These size distributions correspond to the example calibration shown in Figures 3, 5, and S2.

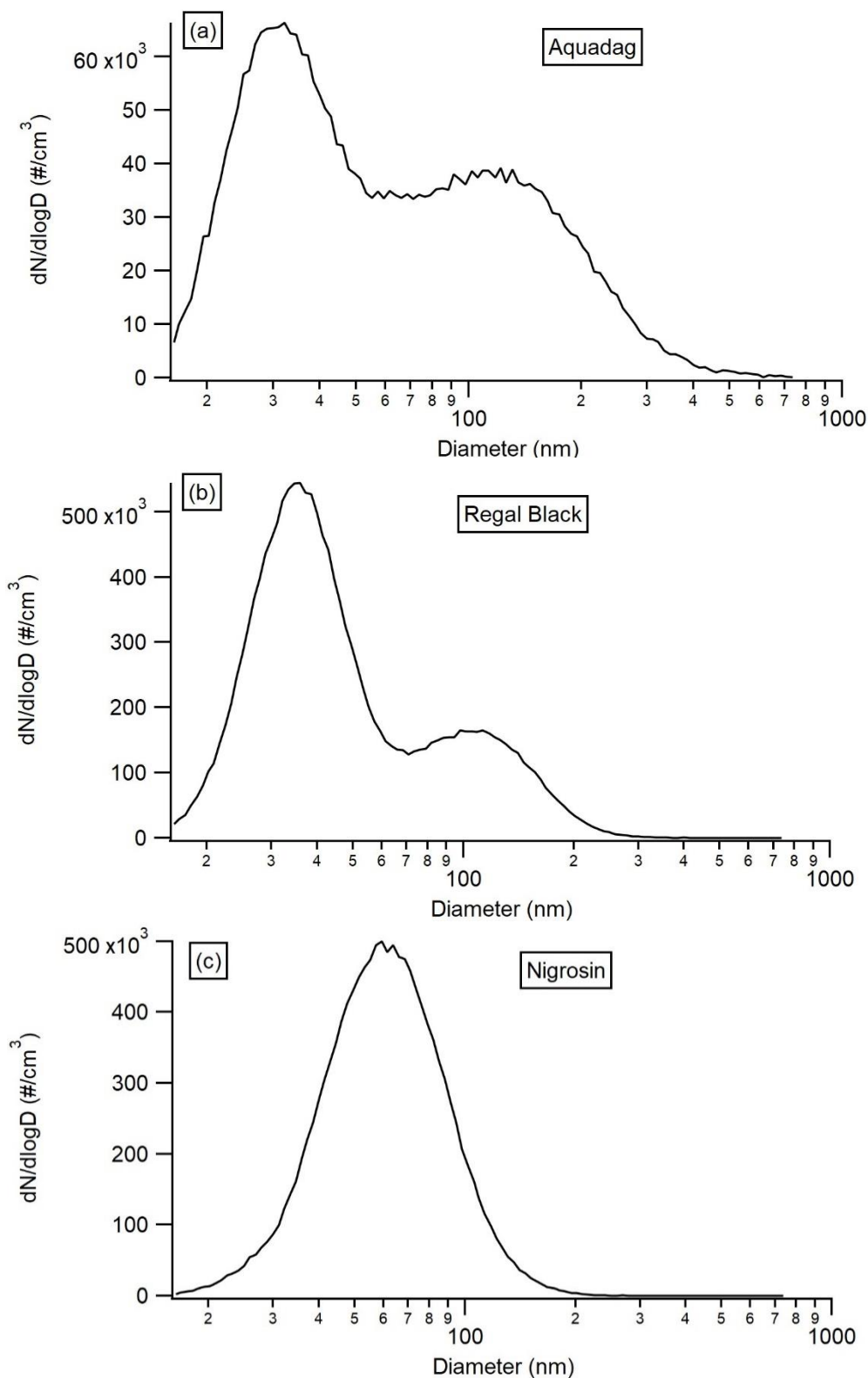


Figure S2: Single scattering albedo at 450 nm (blue) and 660 nm (red) for the three substances: Aquadag (a), Regal Black (b), and Nigrosin (c). All three of these examples correspond to the same data used in figures 3, 5, and S1. Also shown is the Extinction at 450 nm (black). The concentration is varied over the course of the calibration, and the lowest concentrations correspond to the highest noise in SSA calculation. For example, in the bottom panel, the first concentration of Nigrosin corresponds to only 7 Mm^{-1} of Extinction at 450 nm, and 3-4 Mm^{-1} of scattering, resulting in a highly noise estimate of SSA.

