

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 NO<sub>2</sub> 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 NO<sub>2</sub> 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 NO<sub>2</sub> to calibrate is that NO<sub>2</sub> 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 NO<sub>2</sub> 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 NO<sub>2</sub> concentrations are often small enough not to pose a significant health hazard, NO<sub>2</sub> 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<sup>-1</sup> and 5.5 Mm<sup>-1</sup>, respectively. Do the authors have an explanation for non-zero intercepts? In the atmospherically-relevant range for aerosol absorption (0-25 Mm<sup>-1</sup>) such an offset is huge. It is interesting to note that the intercept for nigrosin is < 1 Mm<sup>-1</sup>. 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<sup>-1</sup>, while the smallest is 36 Mm<sup>-1</sup>. 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  $\text{Mm}^{-1}$ ) 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  $10 \text{ Mm}^{-1}$ . 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.

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 ( $\text{Mm}^{-1}$ )	30 second average ( $\text{Mm}^{-1}$ )	60 second average ( $\text{Mm}^{-1}$ )
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.

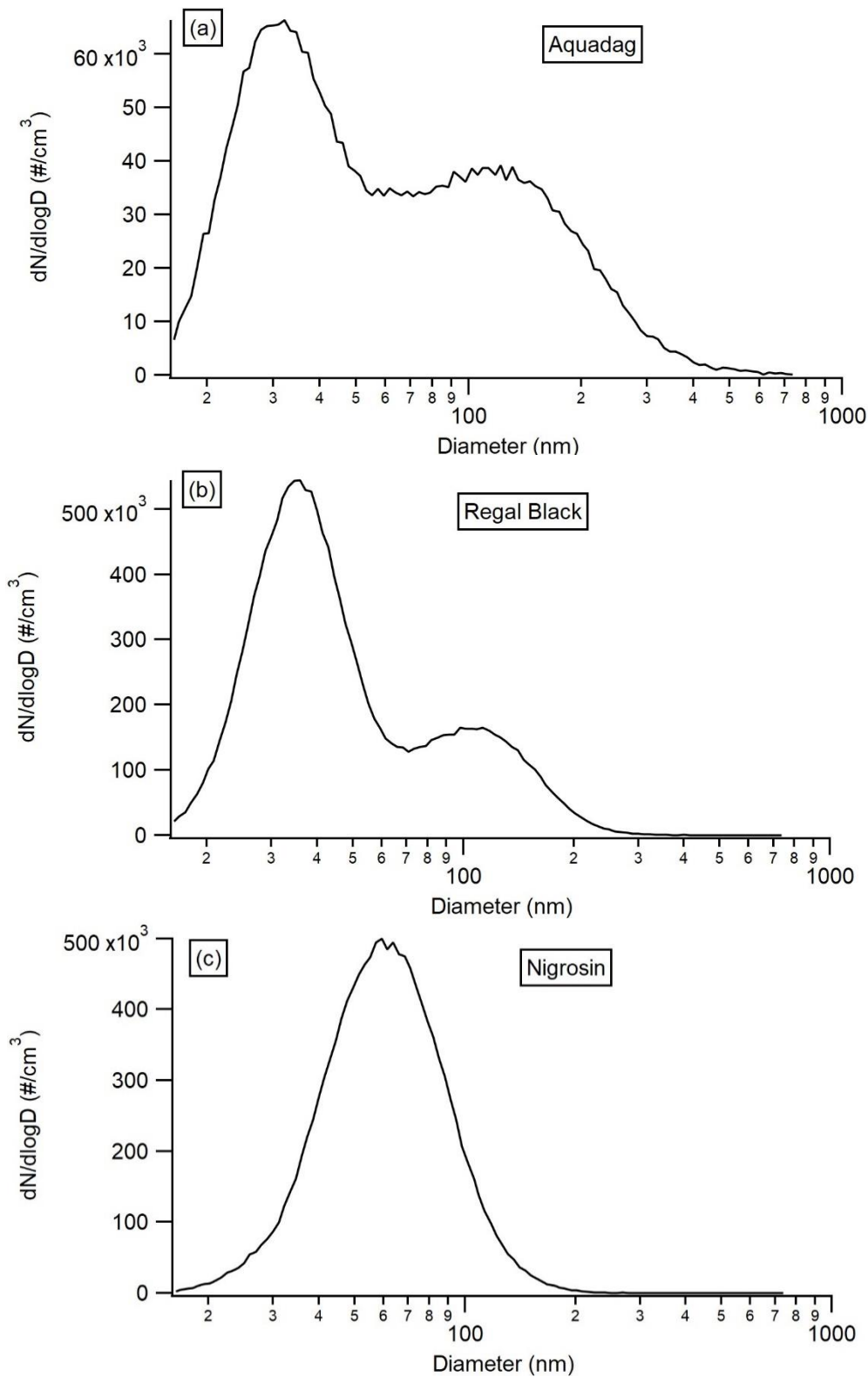


Figure S2: Single scattering albedo at 450 nm (blue) and 660 nm (red) for the three substances: Aquadag (a), Regal Black (b), and Nigrosin (c). All three of these examples correspond to the same data used in figures 3, 5, and S1. Also shown is the Extinction at 450 nm (black). The concentration is varied 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  $7 \text{ Mm}^{-1}$  of Extinction at 450 nm, and  $3\text{-}4 \text{ Mm}^{-1}$  of scattering, resulting in a highly noise estimate of

