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Atmospheric Measurement Techniques Discussions

Interactive comment on "A novel approach to calibrating a photo-acoustic absorption spectrometer using polydisperse absorbing aerosol" *by* Katie Foster et al.

Anonymous Referee #1

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Manuscript: A Novel Approach to Calibrating a Photo-acoustic Absorption Spectrometer using Polydispersed Absorbing Aerosol (Foster et al.,)

Two technical issues continue to plague the part of our research community focused on better quantifying direct radiative forcing by light absorbing aerosols: measurement bias and calibration standards. First there is the well-documented measurement biases with filter-based measurements, such at the PSAP (particle soot absorption photometer) and the Aethalometer than can lead to overestimation of the aerosol absorption. To get around the use of filter-based measurement and their associated measurement bias photo thermal based measurements (e.g., photoacoustic and other photo thermal

techniques) have been developed. However, this class of instrumentation lacks a broad spectrum calibration standard. The manuscript submitted by Foster et al., describes a technique to address the lack of a broad spectrum photo thermal technique calibration standard by combining simultaneous measurements from their photo acoustic absorption spectrometer and a CAPS-SSA monitor (Aerodyne Research Company instrument that measured aerosol light extinction through the cavity attenuated phase shifted technique and scattering via an incorporated integrating sphere.) By taking the difference between the CAPS-SSA reported extinction and scattering values, aerosol light absorption can be extracted and thus used to calibrate the photo acoustic spectrometer. This approach becomes very useful at shorter visible wavelengths (e.g., 405 nm) where useful gas calibration standards are not available. Given that the work described in this manuscript is of value to only those groups that conduct in situ measurements via the photothermal technique, it is highly myopic and the target audience quite small. However, the subject matter and results are certainly well suited for an AMT venue.

This manuscript has a "draft" feel to it. While the data analysis looks solid there 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. 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). And third, 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. Errors of this type along with the sloppy writing has cast a shadow over the entire manuscript, which contains interesting results but that are overshadowed. Therefore, this reviewer recommends that this manuscript be rejected so that the authors go over this manuscript more carefully and thoroughly and then resubmit it for publication - which this reviewer believes will find acceptance.

A couple of additional comments.

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.

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

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) then 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.

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).

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.

Similarly, 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.

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