

Interactive comment on “Calibration of a photoacoustic spectrometer cell using light absorbing aerosols. A technical note” by Nir Bluvshstein et al.

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N. Wagner (Referee#2): The authors discuss and compare the calibration of a multipass aerosol photoacoustic spectrometer at 404 nm using absorbing aerosol and ozone. The main difficulty with using an absorbing aerosol to calibrate a photoacoustic spectrometer is knowing beforehand the single scattering albedo (or complex index of refraction) of the aerosol. The advance presented in this paper is using an independent measurement of the bulk index of refraction using spectroscopic ellipsometry and a Mie scattering calculation to determine the aerosol absorption coefficient of size-selected aerosol which is then used to calibrate the photoacoustic spectrometer. The authors note that the calibrations using absorbing aerosol and ozone disagree by a factor of 2.

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This is an important and somewhat troubling observation as it may affect several instruments currently in use and the interpretation of historic data from these instruments. As such, it is an important result that should be published in AMT.

Reply: We thank Dr. Wagner for the careful reading of the manuscript and for these supporting statements.

The authors leave two important questions unanswered that will be of interest to most readers. First, what is the source of the disagreement between the calibrations? Is the issue specific to the multipass photoacoustic spectrometer, more generally to 404 nm photoacoustic measurement, or does the issue persist with O₃ at longer wavelengths across the visible (532 nm)? Is there a non-thermal absorption process in O₃ that needs to be better understood?

Reply: We currently cannot answer this question because we only have the PAS-CRD-S system at 404 nm wavelength. However, in our understanding there is no known non-thermal absorption process for O₃ at this wavelength.

The authors have likely tried to answer this question and not arrived at a satisfactory answer. While this question does not need to be answered before publication, some more discussion of problems they checked for would be helpful. Here are few experiments that I would like to see the results of. If the authors have already done some of these experiments, including the results would be appropriate. If the instrumentation is available, further checks could be done and discussed. 1) Does the O₃ calibration slope vary with laser intensity in the PAS cell? A stable calibration as the PAS laser power is varied would suggest that O₃ is not destroyed through any photochemical process. It would also demonstrate that the O₃ calibration is not contaminated by NO₂ and its photolysis.

Reply: Additional information related to this issue was added to the supplementary information. We show that the PAS signal to O₃ light absorption is linear with laser power.

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2) Can the authors estimate the possible contamination of the O₃ produced by the discharge or UV lamp (NO₂)? Using either a UV ozone instrument or extinction measurements at variety of wavelengths.

Reply: Currently we do not have sensitive enough NO₂ measurement capability. We took measures and tests to ensure that NO₂ or other contamination if exist is negligible. A discussion on this issue was added to the supplementary information.

3) Does the O₃ calibration curve differ when O₃ is generated using the UV lamp compared with the corona discharge?

Reply: We show in the supplementary material comparison between different calibration curves performed at different instrumental setup and with using the two O₃ generation methods on the same day. Results shows that the calibration slopes differ by less than 5%.

4) Does the O₃ calibration curve agree with the absorbing aerosol calibration at other wavelengths (532 nm, 660 nm) commonly used for photoacoustic spectroscopy?

Reply: Since we currently only have a PA-CRD-S system at 404 nm we cannot answer this question. However, due to the need to measure in the short wavelength spectral range, it is important to understand processes in these wavelengths where potential problems may arise.

5) How do these calibrations compare with an extinction-minus-scattering measurements of absorption?

Reply: We currently do not have nephelometer capable of measuring scattering at 404 nm wavelength so we cannot address this question as well.

Second, what is the total uncertainty with the nigrosin calibrations? Ozone calibrations are attractive (although possibly flawed due the results reported in this paper) in part because the calibration can be linked to common and accurate UV O₃ instruments and the well-measured O₃ cross-section in the UV. The nigrosin calibration is susceptible

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to uncertainty from selection of multiple charge particles in the DMA, uncertainty in the CPC measurement, uncertainty in the nigrosin index of refraction measurement, and uncertainty in applying Mie theory to possibly non-spherical particles. Similar size selected aerosol calibrations for aerosol mass spectrometers are uncertain at the +/- 35% level. The authors should present an overall uncertainty estimate for the nigrosin calibration before final publication.

Reply: Additional discussion regarding the error propagation through the Mie routine and its implication to the PAS calibration curve was added to the main text. Table 1 lists all components of uncertainty propagated used.

Technical comments: Line 123: Does the PAS instrument here use a single microphone or two (subtracted) as described by Lack et al.?

Reply: Two microphones are used in this instrument as described in Lack et al. 6 and in the following line in the text.

Line 191: Please state the manufacturer and batch number the nigrosin used here. Its composition can vary from batch-to-batch, and it is not clear how much the absorption (or index of refraction) vary between batches/manufacturers.

Reply: Nigrosin was purchased from Sigma-Aldrich (batch number: 14828BD). This information was added in the text.

Line 193: inconsistent spelling of 'nigrosine'

Reply: Was changed to 'nigrosin'

Line 285: "PAP instrument" should be "PAS instruments"

Reply: Was corrected

Figure 2: When describing Fig. 2 the author should clearly state the shift in resonant frequency with increasing O₃ concentration is theoretical bias in an theoretical instrument with a much higher-Q acoustic resonator (or calibrations with higher O₃ concen-

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trations than used in this paper), and the observed shift of <1 Hz with not affect the O3 calibration slope reported in this paper.

Reply: The following section was added in the discussion of figure 2: “Although figure 2 demonstrates that no change in Fr could be detected in our instrument with increasing O3 concentration of up to 750 ppm, such a shift due to gas composition change is possible in higher Q acoustic resonator and with higher O3 concentration.”

Figure 3: The authors should report their measurements of the nigrosin index of refraction in tabular form so that other groups can apply this information to photoacoustic calibrations at 404 nm and other wavelengths across the visible. Perhaps as supplemental data.

Reply: The spectroscopic ellipsometry data was added in table S1 of the supplementary material.

Figure 5: For this O3 calibration, is the O3 generated using the discharge, the lamp, or both?

Reply: The O3 used in the calibration curve presented in figure 5 was prepared using the corona discharge O3 generator. This is clarified in the main text with more detailed description of the instrumental setup.

Figure 5: Uncertainties in the slopes and intercepts are unrealistically small and should include an estimation of systematic errors which are likely larger than the mathematical uncertainty associated with the fit.

Reply: Additional sources of error were used and propagated through the Mie routine. These increase the calculated uncertainty of the PAS calibration curve. Figure 5 and the related parts in the text were changed accordingly. However, the results and conclusions remain robust.

Please also note the supplement to this comment:

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<http://www.atmos-meas-tech-discuss.net/amt-2016-323/amt-2016-323-AC2-supplement.pdf>

Interactive comment on Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2016-323, 2016.

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