

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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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
C1

a factor of 2. 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.

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?

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.

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.

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

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

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

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 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.

Technical comments:

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

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.

Line 193: inconsistent spelling of 'nigrosine'

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

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

Figure 3: The authors should report their measurements of the nigrosin index of refraction

fraction 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.

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

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.

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