Interactive comment on “Technical Note: Can ozone be used to calibrate aerosol photoacoustic spectrometers?” by Donald A. Fischer and Geoffrey D. Smith

Anonymous Referee #3

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The authors compare several calibrants for a photoacoustic spectrometer designed for the measurement of aerosol absorption, specifically nigrosine particles, NO2, and O3. Recently, two groups have reported contradictory results calibrating similar photoacoustic spectrometers with O3. The photoacoustic spectrometer presented here uses several wavelengths to excite a single photoacoustic cell (where as previous reports were limited to a single wavelength per photoacoustic cell). Because the calibration is independent of excitation wavelength, calibrations at several wavelengths can be compared in addition to comparison between different calibrants. The authors also use a cold trap to introduce O3 into the photoacoustic spectrometer in the absence of O2. It is in the absence of O2 that authors find dramatic differences in the calibration with O3.

This paper is an important contribution to this ongoing discussion regarding calibration of photoacoustic spectrometers with O3 and is appropriate material for AMT. It is organized and well written. It should be published with a few minor changes.

Comments

1) I suspect that experiments in the absence of O2 are motivated by the reaction to reform O3 (O(3P) + O2 -> O3, JPL Publication 15-10, Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies), however, this reaction is not discussed explicitly nor are the results compared with the known rate of this reaction. The authors should discuss this reaction, and it would be helpful if the authors attempted a simple box model of O3 photochemistry in the PAS cell.

2) In the discussion of photodissociation of O3 by 532 nm light, could the authors estimate the expected loss of O3 based on the residence time in the sample cell, O3 cross section, and assuming 100% yield to the photodisociation channel.

3) Page 2 line 26 – My understanding is that Bluvshtein et al. measured the RI only of the nigrosine independently. For other materials, the RI was retrieved from broadband extinction measurements.

4) Page 4 line 5-8 – Does an absorber need to be present to determine the resonant frequency? Or is a background signal used?

5) Figure 3 – Drifts in the PAS signal are not explained. Do the authors know the source of these drifts?

6) Figure 4a: The peach/orange color trace is mislabeled. I understand it to be 780 nm?

7) Figure 4b: In this figure it seems that the PAS sensitivity in the absence of O2 for 662 and 532 differ by 10-20%, but in figure 2 the calibration slope is nearly the same for 532 nm and 662 nm in N2. Why are they different?
8) Page 9 line 26: A scoping argument against a more thorough explanation. If not here than where? A simple boxmodel including the reaction to reform O3, could answer some of the questions raised here and on pg 6 line 28-29.

9) Page 10 line 14: missing negative in the sentence? I thought the N2 bath gas was “inefficient”?

10) What is the O2 impurity in the N2 gas used? It may be useful to account for any trace O2 in these experiments.