

Interactive comment on “The impact of bath gas composition on the calibration of photoacoustic spectrometers with ozone at discrete visible wavelengths spanning the Chappuis band” by Michael I. Cotterell et al.

Anonymous Referee #3

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Manuscript: The Impact of bath gas composition on the calibration of photo acoustic spectrometers with ozone at discrete visible wavelengths spanning the Chappuis band (Cotterell et al.,)

Referee Review of manuscript

High accuracy/precision measurements of aerosol light absorption continues to be a need as this measurement remains the controlling factor as realizing further reduction in the uncertainty in the aerosol direct radiative forcing contribution to global climate

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change. To this end, in situ techniques have been developed to address measurement bias in filter-based measurements that are reaching their utility limits. Chief among these in situ techniques is the photo-acoustic spectrometer. By directly measuring light absorption through the photo thermal effect, the PAS can provide a high accuracy measurement of aerosol light absorption. The “rub” is having a high accuracy calibration. To this end, PAS calibrations have utilized diluted NO₂ in air (or N₂) and ozone in the RGB spectral range. However, with improvement in PAS measurement precision and because of growing need to better quantify the contribution of brown carbon (BrC) to aerosol absorption, new demands on improved measurement accuracy has arisen. But to address this need, improvement of the measurement accuracy of the calibration standard is needed. For example, while NO₂ works quite well at the green wavelengths, a photodissociation pathway limits the utility of this cal gas at 405 nm (a popular emission wavelength). The present study aims at tackling this gap by furthering the work of Fischer and Smith (2018) using ozone at the RGB wavelengths by carefully defining the PAS calibration conditions on bath gas.

As one trained in chemical physics I particularly enjoyed the favor of this paper. As a matter of fact, this manuscript would easily fit in a journal of chemical physics. But, as the purpose of this work is to alert our aerosol community to the subtle but important consequences that bath gases have on energy transfer efficiency, and, in turn, on the overall accuracy of the PAS measurement, this manuscript is perfectly appropriate for AMT. This manuscript is very well written and thorough in its analysis, and thus deserves to be published. My comments are of a minor variety which can be readily corrected.

Page 2. Line 19: While discussing the measurement bias associated with the PSAP, the authors cite the Lack et al., study which reported a bias that ranges from ~50 - 80%. The authors could go a bit further and state that this bias exhibits an OA/BC dependence. While certainly not the focus of this paper, from a completeness point-of-view, citing this helps point to where some of the filter-based measurement bias likely

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originates from.

Page 3; Line 15: The authors write "...large NO₂ absorption cross section range causes saturation in the 405-nm spectrometers for concentrations..." This is a bit misleading. The primary issue for the use of NO₂ at 405 nm is that a photodissociation pathway opens up at wavelengths $< \sim 420$ nm. (See for example, Gardner et al., JGR 92 1987.) Please reword this to better reflect that photodissociation is what limits the use of NO₂ as a cal standard at 405 nm. Besides, the reason put forth by the authors that one must use the same concentration to calibrate both the red and blue channels sounds more like a strawman argument.

Page 9, line 7: What is the nominal signal level of the background contribution (Sbg-corr) to the overall PAS signal. I'd like to have a sense of how great this background correction is. Presumably, since this contribution is constant irrespective of the aerosol loading, depending upon the background signal amplitude, this contribution could be more important at lower signal levels. Are we talking about $S_{bg-corr} = 0.1 \text{ Mm}^{-1}$ or 1 Mm^{-1} or $10s \text{ Mm}^{-1}$. I would like to have my fears allayed that in the limit of weak aerosol absorption signal (the atmospherically relevant situation) that the reported PAS signal for the aerosol is not the result of subtracting two big numbers to get a small number.

At the risk of being a bit pedantic, could you please reorder the legend on Figure 3b. As currently displayed, the traces are solid, dotted, and dashed, while the legend is solid, dashed, and dotted. This is certainly a cosmetic request, but makes it easily for the reader. Also, are error bars present on the PAS signal (and are just too small to be observed on the plot scale) or are they not present. If the latter, please add.

This reviewer is most intrigued by the potential consequences of reduced pressure at aircraft sampling altitudes on quenching rates. The authors kick this can down the road but this could be quite interesting from both a fundamental energy transfer perspective as well as a practical aspect. Staying with this theme, I cannot help but wonder if NO₂

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as a calibration gas - available with either N₂ or air as the bath gas - might also exhibit a similar quenching sensitivities to differing bath gas mixtures as displayed by ozone. As highlighted above, one would expect that bath gas quenching could shift the quantum yield for NO₂ photodissociation at 405 nm.

The last request, which the authors are encouraged to do, but certainly not required given the target audience. It would be nice to add a figure displaying the potential energy surfaces (even as a simple 2-D plot) for the various O₃ dissociation pathways. This is certainly the chemical physicist in me requesting this as that is how I can readily see what is going on. For those researchers not accustomed to chemical physics, such a figure would help clarify the subtle pathways present in ozone.

Interactive comment on Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2018-409, 2018.

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