Review of 'Technical Note: Can ozone be used to calibrate aerosol photoacoustic spectrometers?', by Fischer and Smith, 2018.

Summary and General Comments

Photoacoustic spectrometers (PAS) require an accurate calibration for subsequent measurements of absorption. Fischer and Smith add to an ongoing discussion concerning the accuracy of PAS calibrations with ozone for applications pertaining to aerosol absorption measurements at laser wavelengths in the visible spectrum. To put this work in context, numerous researchers have used O_3 to calibrate PAS for aerosol absorption applications. However, Bluvshtein *et al.* reported a factor of two discrepancy between their O_3 calibration and that performed with an aerosol (nigrosin dye) calibrant at a PAS laser wavelength of 405 nm.[1] Meanwhile, a subsequent paper by Davies *et al.* reports excellent agreement between an O_3 calibration and that attained using nigrosin dye at multiple PAS laser wavelengths,[2] including the same 405 nm wavelength reported in the Bluvshtein *et al.* work. Bluvshtein *et al.* could not ascertain the source of their calibration discrepancy for using an O_3 calibrant and, as the current authors' state, further investigation into the accuracy of O_3 calibrations of PAS is warranted. Fischer and Smith first assess the impact of photodissociation at a 532 nm wavelength on the measured PAS response and then investigate how PAS sensitivity factor depends on the mole fraction of O_2 (x_{O2}) in the bath gas. In a pure N_2 bath gas, the PAS response is reduced by 5% when a continuous output 532 nm laser irradiates the gas sample simultaneous to a PAS modulation laser of 662 nm wavelength, while this loss in PAS response is negated by adding O_2 to the bath gas even at small $x_{O2} = 0.05$ concentrations. Notably, the PAS sensitivity factor is measured at 532, 662 and 780 nm with variation in the O_2 and N_2 mole fractions in the bath gas. The PAS sensitivity factor increases with x_{O2}, approaching a plateau at $x_{O2} > 0.2$ and is in near-exact agreement with an NO_2 and nigrosin aerosol calibration for $x_{O2} = 1$. However, the PAS sensitivity of the O_3 calibration for x_{O2} close to zero is almost a factor of 3 smaller than that of the NO_2 calibration and is attributed to N_2 being very inefficient (compared to O_2) at converting the energy of excited O_3 to thermal energy through collisional relaxation. Ultimately, this work does not resolve fully the discrepancies between the Bluvshtein *et al.* and Davies *et al.* studies, but is a new and important contribution to the ongoing discussion of O_3-based PAS calibration, raising the important consideration of bath gas composition. Moreover, Atmospheric Measurement Techniques is a suitable location for this work. Therefore, I recommend the publication of this Technical Note after the following comments have been addressed.

Specific comments

Page 1 line 18: The authors highlight the work of Bluvshtein *et al.* and Davies *et al.* in the abstract as partly motivating the current study. Therefore, the authors should summarise how the current work may reconcile these two studies, if at all, at the end of the abstract. As discussed further below, the authors incorrectly state in their conclusions that both the Bluvshtein *et al.* and Davies *et al.* studies use a bath gas of 10% O_2 in N_2; while this is the case for the Bluvshtein study, the Davies study is for ozone injected into ambient air (25% O_2 in N_2). These key differences in bath gas composition may partly account for calibration discrepancies between the two studies.

Page 1 line 25: Some readers may not be familiar with a 'multipass enhancement cell'. The authors should make clear at this early stage what is meant by 'multipass' (i.e. multiple reflections of the excitation laser beam through the sample), although it is acknowledged that specific details of the multipass optical cell is given on page 3 line 11 – page 4 line 1.

Page 2 line 1: '…recent works exploring its validity have come to contradictory conclusions' should emphasise that these works were for visible laser wavelengths, i.e. '…recent works exploring its validity at visible wavelengths have come to contradictory conclusions'.

Page 2 line 2: '…discrepancy between ozone calibrations and particle-based calibrations'. The authors should state that this study was at a PAS laser wavelength of 405 nm only.

Page 2 line 16: 'Most commonly, this…'. 'This' is ambiguous and perhaps should read, 'Most commonly, this sensitivity factor…'.

Page 2 line 25: Replace '…light absorbing aerosols' with '…size selected light absorbing aerosols'.

Page 2 line 27 - 28: Replace 'when they performed a calibration with ozone' with 'when they performed a calibration with ozone at a laser wavelength of 405 nm'.

Page 2 line 29: Add after 'Mie theory', 'at laser wavelengths of 405, 514 and 658 nm'.

Page 2 line 32: The authors should state here: 'However, we note that the O_3 calibrations performed by Bluvshtein *et al.* were in a bath gas composed of 90% N_2 and 10% O_2, while the calibrations of Davies et al. were performed in a bath gas of ~75% N_2 and 25% O_2 (with an ozonated oxygen flow added to ambient air).'

Page 3 line 3 – 4: '…observe a much lower sensitivity with ozone calibrations.' This is a particular strong statement, in light of the authors' results, to suggest the sensitivity is much lower. The statistically-significant lower sensitivity occurs only when $x_{O2} < 0.2$. Indeed, the O_3 calibration agrees near-exactly with that using NO_2 and aerosol-based calibrations when x_{O2} approaches one.

Page 4 line 20: For the purposes of future work on calibrations by other researchers, further experimental details should be given here. Such details include the pressure and temperature of the sample in the PAS cell. Was the NO_2-laden N_2 pushed or pulled through the sample line? What was the total flow rate through the spectrometers? What was the 662 nm laser power, as measured by the photodiode?

Page 4 line 29: Again, further details should be given here. What powers did the lasers have, as measured by photodiode, during measurements? This quantity is very important given the photolysis observed by the authors. What was the pressure and temperature of the sample in the PAS cell? Was the O_3-laden sample pushed or pulled through the PAS and CRD? What was the total flow rate through the spectrometers?

Page 5 line 7: What is the particle cut diameter for a 0.57 millimetre orifice? Moreover, is 0.57 mm a diameter or radius?

Page 6 lines 11-13: Here, it is important to note that (i) the O_3 calibrations were only done at 532 and 662 nm, with the 406 nm PAS signal (which is of most relevance to the Bluvshtein study) showing, presumably, very little response to the O_3 concentrations generated. (ii) The calibration coefficient quoted is that for the fit through both the 532 and 662 nm calibration data.

Page 6 line 17: The sensitivity here is the average of 532, 662 and 780 nm data. It would be useful to have the calibrations for the individual wavelengths. Indeed, the 662 nm calibration in Figure 2 appears to agree with the sensitivity of the NO_2 calibration, while the 532 nm sensitivity is lower.

Page 6 line 28: 'it can be convenient to calibrate in air…'. Emphasise here that this is exactly the case for the Davies *et al.* study. I think it is important to remind the reader of the Bluvhtein and Davies studies to put the current work in context.

Page 6 line 31: The reader is directed to Figure 4A. Why are there two series for 662 nm on this plot? Presumably, one of the series (the light red line) is actually for the 780 nm wavelength?

Page 7 line 11: The reader is now directed to Figure 4B. It is not clear what the different data series are. Please could the authors add a legend.

Page 9 line 2: The authors have now clearly demonstrated a significant impact of bath gas composition on PAS sensitivity. It would be useful at this point to put this result in context with their motivation for this study. The authors should again highlight the differences in O_2 composition for the Bluvshtein (10%) and Davies (25%) studies, and provide estimates of the approximate biases in calibrations that use these bath gas compositions. From the data here, it seems that the biases would be around 17% and 8% for x_{O2} values of 0.1 and 0.25, respectively (assuming the PAS sensitivity behaviour at 405 nm is similar to the data measured here at longer visible wavelengths). Therefore, the current study into bath gas effects does not explain fully the factor of two discrepancy reported by Bluvshtein *et al*., but is expected to be a significant contributor.

Page 9 lines 6 – 7: 'excited state of the bath gas' should perhaps read 'excited state of the analyte'.

Page 10 line 2: 'as long as it is performed with 100% O_2 as the bath gas.' This statement seems unjustified as the authors data suggests that PAS sensitivity factors similar to that measured for NO_2 calibrations are found even at x_{O2} values of ~0.17 when uncertainties in both the O_3 and NO_2 PAS sensitivities are considered. Certainly, though, the calibration coefficient markedly drops for x_{O2} <0.1.

Page 10 lines 14 – 16: This sentence is not correct. Bluvshtein *et al*. use the values as currently quoted, but Davies *et al.* use an O_3 laden oxygen flow and add to air giving a PAS cell bath gas composition of approximately 25% O_2 and 75% N_2. These differences in bath gas composition should be stated clearly with estimates of the PAS calibration biases expected from the current study. Clearly, the current study does not completely reconcile the discrepancy.

References

1   N. Bluvshtein, J. M. Flores, Q. He, E. Segre, L. Segev, N. Hong, A. Donohue, J. N. Hilfiker and Y. Rudich, *Atmos. Meas. Tech.*, 2017, **10**, 1203–1213.

2   N. W. Davies, M. I. Cotterell, C. Fox, K. Szpek, J. M. Haywood and J. M. Langridge, *Atmos. Meas. Tech.*, 2018, **11**, 2313–2324.