

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

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1. Page 1 line 18: The authors highlight the work of Bluvshstein 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 Bluvshstein et al. and Davies et al. studies use a bath gas of 10% O₂ in N₂; while this is the case for the Bluvshstein study, the Davies study is for ozone injected into ambient air (25% O₂ in N₂). These key differences in bath gas composition may partly account for calibration discrepancies between the two studies.

C1

We appreciate this suggestion and have added a sentence at the end of the abstract briefly addressing this.

2. 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.

We have added a brief explanation of what a multipass enhancement cell is at this point.

3. 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’.

We made this change.

4. 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.

We made this change, also.

5. Page 2 line 16: ‘Most commonly, this...’. ‘This’ is ambiguous and perhaps should read, ‘Most commonly, this sensitivity factor...’.

We clarified this sentence by referencing the symbols used in Eq. 1.

6. Page 2 line 25: Replace ‘...light absorbing aerosols’ with ‘...size selected light absorbing aerosols’.

We made this addition.

C2

7. 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'.

We changed the sentence to reflect Bluvshstein et al. used a 405 nm laser.

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

This has been added at that point in the manuscript.

9. Page 2 line 32: The authors should state here: 'However, we note that the O₃ calibrations performed by Bluvshstein et al. were in a bath gas composed of 90% N₂ and 10% O₂, while the calibrations of Davies et al. were performed in a bath gas of ~75% N₂ and 25% O₂ (with an ozonated oxygen flow added to ambient air).'

We thank the reviewer for making this suggestion, and have copied it into the manuscript.

10. 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 xO₂ < 0.2. Indeed, the O₃ calibration agrees near-exactly with that using NO₂ and aerosol-based calibrations when xO₂ approaches one.

We have changed this to read "...observe a lower sensitivity with ozone calibrations."

11. 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 NO₂-laden N₂ 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?

We appreciate this suggestion. We have provided some more detail here. See the comment under Page 4 line 29 (below) for more information on the laser power.

C3

12. 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 O₃-laden sample pushed or pulled through the PAS and CRD? What was the total flow rate through the spectrometers?

We appreciate this suggestion. We have provided some more detail here, including details about T and P. The incident beam powers have been listed under the instrument description. The multipass powers (those measured by the photodiode) are effective powers – they are relative, not absolute, as the PD calibration includes losses from windows and other optics.

13. 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?

Thanks for pointing out our typo. It should have read "0.071 mm". We have also included the cut point (~ 1100 nm) for the orifice used.

14. Page 6 lines 11-13: Here, it is important to note that (i) the O₃ calibrations were only done at 532 and 662 nm, with the 406 nm PAS signal (which is of most relevance to the Bluvshstein study) showing, presumably, very little response to the O₃ concentrations generated. (ii) The calibration coefficient quoted is that for the fit through both the 532 and 662 nm calibration data.

Actually, calibrations were performed at 532, 662, and 780 nm. We did not include 406 nm calibrations because of the low signal for that wavelength at the ozone concentrations used. We have added text here to clarify points (i) and (ii) and added text in the Ozone Calibration Methods section to clarify which wavelengths were used.

15. 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 NO₂ calibration,

C4

while the 532 nm sensitivity is lower.

We have added the sensitivities derived from fitting the individual wavelengths as well for easier comparison. They differ by no more than 7%.

16. 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 Bluvshstein [sic] and Davies studies to put the current work in context.

We added a reference to Davies et al. here.

17. 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?

Thank you for pointing this out. The reviewer is correct, and we have corrected the plot accordingly.

18. 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.

We have added a legend to Figure 4B.

19. 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 O₂ composition for the Bluvshstein (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 xO₂ 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 Bluvshstein et al., but is expected to be a significant contributor.

C5

We thank the reviewer for this helpful suggestion. We have added explicit discussion of how the findings from the current study might apply to the work of Bluvshstein et al. and Davies et al. Specifically, we point out that the O₂ content of the bath gas does not seem to reconcile the discrepancy between these two studies.

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

Actually, in this case we were in fact referring to the bath gas. However, this brings up a good point: Any long-lived excited state, whether it be the analyte, the bath gas, or an intermediate, would have a similar effect. We have added language to this effect here.

21. Page 10 line 2: 'as long as it is performed with 100% O₂ as the bath gas.' This statement seems unjustified as the authors data suggests that PAS sensitivity factors similar to that measured for NO₂ calibrations are found even at xO₂ values of ~0.17 when uncertainties in both the O₃ and NO₂ PAS sensitivities are considered. Certainly, though, the calibration coefficient markedly drops for xO₂ <0.1.

Yes, we agree with the reviewer. However, we note that (disregarding uncertainties) there is a slight upward trend in the data toward $\chi = 1$. Although we cannot say whether this trend is "real" due to uncertainties, we prefer to err on the side of caution and recommend 100% O₂ as the calibrant.

22. Page 10 lines 14 – 16: This sentence is not correct. Bluvshstein et al. use the values as currently quoted, but Davies et al. use an O₃ laden oxygen flow and add to air giving a PAS cell bath gas composition of approximately 25% O₂ and 75% N₂. 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.

Thank you for pointing out our error. We've fixed this error and added estimates of the

C6

effect for each study.

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