

## ***Interactive comment on “On the accuracy of aerosol photoacoustic spectrometer calibrations using absorption by ozone” by Nicholas W. Davies et al.***

### **Anonymous Referee #1**

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Davies et al. (2018) present work on calibrating photoacoustic spectrometers using ozone, and compare aerosol optical properties determined using the ozone calibrations to optical properties measured using a different method. The author find that the ozone calibration works well at 405 nm, and that the measured absorption coefficients for nigrosin aerosol agree well with absorption coefficients calculated using refractive indices derived from ellipsometry. This is in contrast to previous work that found that using ozone to calibrate the PAS resulted in absorption coefficients twice as large as those derived from the ellipsometry measurements. Additionally, unlike the previous work, the authors performed experiments at three wavelengths, and found excellent agreement at all three wavelengths. This is a valuable study, and I recommend that it

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be published in AMT.

My main concern is that no effort was made to verify that ozone was the only source of extinction/absorption in the CRDS and PAS cells. While the agreement at all three wavelengths between the measured aerosol absorption and the absorption calculated using the previously measured refractive indices argues against an interference, it would be nice to have some additional checks, such as measuring the particle number concentrations during the ozone calibration, measuring the ozone by an independent method and comparing the extinction calculated using that concentration to the measure extinction, or putting the same ozone flow into the blue and red CRDS cells and making sure the concentrations calculated using the literature cross sections agree. This last check will be somewhat tricky due to the large difference in the ozone cross sections, but it should be possible in the 30-50 ppmv range, and it would provide a nice check to ensure that there are no other sources of extinction such as NO<sub>2</sub> (or possibly another absorbing gas) or aerosol particles in the cells. For the 405 channel, reversing the order of the CRDS and PAS cells could also be tried.

I recognize that the authors may not have all the equipment needed to perform some of these experiments (e.g. an ozone monitor), and so not all of these experiments need to be performed prior to publication. However, the authors should be able to do some of these checks using the data they already have (such as comparing calculated ozone concentrations from the blue and red CRDS), and given the discrepancy between this study and the study by Bluvshstein et al. (2017), it would be nice to see these additional checks performed to help investigators going forward.

### **Specific comments:**

1. P2L29-P3L5: Somewhere in the introduction or possibly in the discussion section it would be good to mention the recent work by Cremer et al. (2017), who found

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that the photoacoustic response was lower than would be expected based on Mie calculations, and how those results relate to yours.

2. P4L9-10: "The cell was positioned within a multi-pass optical system formed by two cylindrical mirrors. . ." Approximately how many passes does the laser make? Also, it should be mentioned that the concavities of the two mirrors are rotated 90° to each other.
3. P4L12: How did you measure the laser wavelengths and line widths?
4. P4L15: What is the manufacturer and part number for the microphones?
5. P4L23-25: "Aerosol absorption coefficients ( $m^{-1}$ ) measured by the photoacoustic spectrometers were converted to absorption cross sections ( $m^2$ ) for comparison to theoretical calculations by dividing by the aerosol number concentrations reported by a CPC (see Sect. 2.4)." I interpret this to mean you divided the measured absorption by the measured concentration, without correcting for the presence of multiply charged particles. If so, these cross sections should be referred to as **effective** cross sections, since the cross sections you would get from this method are going to be larger than what you would calculate from Mie theory due to the presence of multiply charged particles. There are several other places where this applies.
6. P4L26-27: "Cavity ring-down spectroscopy is a highly sensitive technique used for measuring the optical extinction coefficient of gases and particulate matter (O'Keefe and Deacon, 1988; Romanini et al., 1997) without the need for instrument calibration." I'm not sure it's 100% correct to say that CRDS does not require calibration (e.g. Toole et al., 2013). The raw CRDS signal also needs to be adjusted to take into account  $R_L$ , which can require calibration (see below).
7. P4L32: Please provide ring-down time constants for the two CRDS channels.

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8. P5L3-4: What is the radius of curvature of the CRDS mirrors?
9. P5L12-13: "Cavity mirror-to-mirror lengths ranged from 371-423 mm yielding  $R_L$  factors in the range 1.150-1.173." How were the  $R_L$  values measured? While determining  $R_L$  using the physical dimensions of the CRDS cell may be appropriate for aerosol particles (Langridge et al., 2011), Fuchs et al. (2008) found that for gases  $R_L$  was not equal to the geometric  $R_L$ . Were any experiments performed to determine if  $R_L$  in your system is different for gas and particles?

Is there a reason for the different cavity lengths?

10. P5L14-15: See comment 5.
11. P5L20: Were the CRDS cells made of teflon or metal? If they were metal, please specify the material.
12. P6 Figure 1: This figure was hard to understand at first because I expected the colors of a given box to correspond to the wavelength of that instrument. I think the figure would be clearer if the colors of the PAS and CRDS cells corresponded to the wavelength used for that cell. Perhaps then use different shapes to differentiate between the CRDS and PAS cells?
13. P6L7: "...the measured ozone concentrations were used directly." How were the ozone concentrations measured (see comment below), or do you mean measured extinctions were used directly?
14. P6L13-14: "At the start of each calibration cycle, pure oxygen was introduced into the PAS cells through the ozone manifold. The oxygen displaced a fraction of the filtered-air flow through each cell. . ." This sentence and Eq. 2 imply that the flow through the system was a mix of air and gas from the ozone generator. Is this correct? If so, what fraction of the flow came from the ozone generator? How was the ambient air filtered?

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15. P6L20: "The 515 nm PAS cell. . ." Isn't the wavelength 514 nm?
16. P6L21-22: "Ozone splitting ratios derived using this method compared extremely well to in-line mass flow measurements and were in the range 2-28%." What do you mean by "2-28%." Do you mean that the difference in the flow between two cells was between 2 and 28%, or that the splitting ratio,  $\Delta\nu$ , calculated from Eq. 2 was between 2 and 28%?
17. P7L7-9 and P8 Figure 3: "Ozone concentrations in the range  $\sim 10$ -500 ppm were used." How did you determine the ozone concentrations? Figure 3 shows a maximum extinction of  $27 \text{ Mm}^{-1}$  at 405 nm. If this is only from ozone, this gives an ozone concentration of  $\sim 660$ -750 ppmv ( $\sigma_{\text{ozone}}$  around 405 nm is  $1.45 - 1.65 \times 10^{-23} \text{ cm}^2$ , depending on the exact wavelength (Serdyuchenko et al., 2014)), higher than the 500 ppmv in the text. Also, 10 ppmv of ozone gives an extinction of  $\sim 50 \text{ Mm}^{-1}$  at 658 nm. Did you put lower ozone concentrations into the green and red PAS cells to extend the calibration curves to lower values?

Were the same ozone levels used for both the 405 and 658 CRDS channels? If so, how do the ozone concentrations calculated using the measured extinction and the literature cross sections compare for those two wavelengths?

18. P7L17 (Eq. 3): Why is the resonant frequency represented by  $\nu$  in this equation, and  $F_r$  in Eq. 2?
19. P7L18: How is  $P_L$  measured? By the photodiode? Also, what are typical quality factors for your instrument?
20. P8L1 (and elsewhere): I might consider replacing "gradient" with the more common "slope," but this is mostly preference on my part.
21. P8 Figure 3: The y-axis units are inverse megameters ( $\text{Mm}^{-1}$ ), while the units in the text (e.g. P4L23 and P5L9) are inverse meters ( $\text{m}^{-1}$ ). Since  $\text{Mm}^{-1}$  are the

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customary units in aerosol work, I would suggest changing the units in the text, but whatever you choose, the units should be consistent.

22. P8L10: Why was the red CRDS used to calibrate the green PAS? Do you get the same result if you use the blue CRDS instead?
23. P8L17: Please provide the product number and lot number for the nigrosin used.
24. P9L2: What was the DMA sheath flow?
25. P9L11: "The aerosol flow was split between optical cells using a series of Y-flow splitters." Please show how this was done in Figure 1.
26. P12 Figure 5e-f: When I use either the Bohren and Huffman Mie codes or an online Mie calculator ([https://omlc.org/calc/mie\\_calc.html](https://omlc.org/calc/mie_calc.html)) to calculate absorption cross sections, I get numbers lower than those shown in Figure 5e. For example, for 1000 nm diameter particles, I get the following absorption cross sections:  $1.01 \times 10^{-12} \text{ m}^2$  at 405 nm;  $1.06 \times 10^{-12} \text{ m}^2$  at 514 nm; and  $1.10 \times 10^{-12} \text{ m}^2$  at 658 nm. The absorption cross section that I calculate for 400 nm particles at a wavelength of 514 nm ( $1.69 \times 10^{-13} \text{ m}^2$ ) is higher than the value shown in Figure 5f ( $\sim 1.4 \times 10^{-13} \text{ m}^2$ ) Please explain these discrepancies. If there was an error in the Mie calculation, how does this affect the agreement between the measured and modeled aerosol extinction and absorption cross sections?
27. P12L19-20: See comment 5.
28. P13 Figure 6 and P14 Figure 7: Are the measured cross sections effective cross sections (measured extinction or absorption divided by the particle concentration) or are they corrected for the effect of multiply charged particles?
29. Supplementary material, Tables S1 and S2: What do "gdry," "rtd," "btd," and the other abbreviations in the second column of Table S2 stand for? I'm assuming

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that these are the names of the different CRD/PAS cells. If so, the names in the text, in Figure 1, and in the supplement should all be consistent.

30. Supplementary material, Table S2: I'm assuming that "bdry" and "btd" refer to the two 405 PAS cells. If so, why is the gradient for the bdry/bdry PAS/CRDS calibration 25% higher than the gradient for the btd/bdry PAS/CRDS calibration (and the same for rtd/rdry and rdry/rdry)? If you put the blue CRDS in front of PAS 1 instead of PAS 5, do you get the same gradients?

#### Technical corrections:

- P2L34, P3L30, P4L3, P5L14, P11L28 (and possibly other places): There's an extra comma after the "et al." in the in-text citation, e.g. Bluvshstein et al., (2017) should be Bluvshstein et al. (2017).
- P2L29 and P17L33: The second "m" in McManus should be capitalized.
- P16L31-32, P17L33-34: Please provide the DOI for these references (and any other references where the DOI was omitted).

#### References

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