On the accuracy of aerosol photoacoustic spectrometer calibrations using absorption by ozone

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We would like to thank the reviewers for taking the time to read our manuscript thoroughly and for highlighting some important issues, which will be addressed in turn below.

Review 1

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

We have added the following to the manuscript (P2L29-31):

"Biases associated with PAS include a lack of proportionality between the photoacoustic signal and the aerosol absorption cross section for particles with radii greater than 0.7 μm (Cremer et al., 2017). This is not an issue for the current study, which uses an impactor to remove particles with radii > 0.5 μm; see Sect. 2.4."

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.

We have added the following to the manuscript (P4L16):

"The concavities of the two mirrors were rotated 90° to each other."

We have also added the following to the manuscript (P4L22-27):

"In an optimally aligned system, the laser would pass through the acoustic resonator 182 times (Silver et al., 2005; Lack et al., 2012). However, no effort was made to achieve this limit in the current system. Alignment was conducted by visual inspection of the spot pattern only, which almost certainly resulted in a lower number of passes. Quantifying the number of passes through the resonator was not critical. Light exiting the resonator was measured using a photodiode,

which allowed the PAS signal to be corrected for any laser power or alignment instability (Lack et al., 2012).”

3. P4L12: How did you measure the laser wavelengths and line widths?

We have added the following to the manuscript (P4L19-20):

“Laser wavelengths and line widths were measured using an Avantes spectrometer (CompactLine) for the blue and green wavelengths and a Hamamatsu spectrometer (C11697MB) for red wavelengths.”

4. P4L15: What is the manufacturer and part number for the microphones?

We have modified the following in the manuscript (P4L27-29):

“The acoustic signal was detected using microphones (Knowles Acoustics, EK-23132) positioned half way along the lengths of each resonator to coincide with the pressure antinode corresponding to the lowest-order (n = 1) acoustic eigenmode of the photoacoustic cell.”

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.

The reviewer has interpreted this correctly. Although we define ‘ensemble cross sections’ further into the manuscript, it is important to highlight this here too. Hence we have reworded this in the manuscript (P5L3-8) such that it now reads:

“Aerosol absorption coefficients (Mm^{-1}) measured by the photoacoustic spectrometers were converted to ensemble 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). The ensemble absorption cross section represents the mean of the absorption cross sections corresponding to a range of particles sizes, for example from multiply charged particles (see Sect. 2.5). The ensemble absorption cross section is hereafter referred to as the absorption cross section.”

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).

This is a good point and a nice study by Toole et al. (2013), which eliminates some uncertainty in DMA size-selected diameters and CPC uncertainties by effectively calibrating their CRDS. Hence, we have reworded the sentence in the manuscript (P5L10-11) such that it now reads:

"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)."

Please see comment 9 for details regarding determination of the CRDS R_L factor.

7. P4L32: Please provide ring-down time constants for the two CRDS channels.

We have added the following to the manuscript (P5L27-30):

"The τ_0 times for both the 405 and 658 nm CRDS channels used in this study were measured before and after experiments where aerosol was passed through the optical cavities. These τ_0 varied over time by only a small amount due to changes in cavity alignment, cleanliness and the sample pressure. However, typical representative times were 23.1 μs (405 nm) and 34.2 μs (658 nm)."

8. P5L3-4: What is the radius of curvature of the CRDS mirrors?

We have modified the following in the manuscript (P5L17-19):

"Cavity mirrors were manufactured from fused silica with wavelength-specific coatings, 25 mm diameter, 1m radii of curvature and reflectivities in excess of 99.99 % (Layertec GmbH, red 660 nm; CVI Laser Optics, blue 405 nm)."

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?

We have modified the following sentence (P5L30-31):

"Cavity mirror-to-mirror lengths ranged from 371–423 mm yielding geometric R_L factors in the range 1.150–1.173."

The following was also added to the manuscript (P5L31-P6L7):

"The R_L factor appropriate for aerosol measurements was determined from the geometric dimensions of the detection cell. As highlighted by Fuchs et al. (2008), the R_L factor for detection of gaseous species can be different from this value, due to the ability of gaseous samples to diffuse. We determined the gaseous R_L factors by measuring the change in the ring-down times for filtered air plus ozone in (i) standard operation whereby ozone partially diffuses into the volume between the sample inlet and mirror and (ii) non-standard operation whereby ozone was fully mixed into the volume between the sample inlet and mirror by pulling the ozone-laden air out of the cavity through the mirror purge lines. This resulted in R_L factors 1.05 (658 nm) and 1.04 (405 nm)."

Whilst propagating the ozone R_L factors through the calibration procedure did not impact on the overall result of this study, the mean gradients in Figure 7 changed from 0.98 ± 0.01 to 1.08 ± 0.01. Figure 7 has been updated accordingly in the manuscript. Also, the following has been modified in the manuscript (P15L12-15):

"The mean gradient between the modelled and PAS-measured absorption cross sections for nigrosin for all five ozone-calibrated PAS cells was 1.08 ± 0.01 (2σ fitting uncertainty) as shown in Fig 7. Gradients for the 405, 514 and 658 nm wavelengths were 1.08, 1.07 and 1.09 respectively."

The following has been modified in the manuscript (P17L4-6):

"Using nigrosin aerosol with mobility-selected diameters in the range 250–425 nm, we verified that the measured absorption cross sections using photoacoustic spectroscopy agreed with modelled values to within 8 %. "Our result is robust for the optical wavelengths 405, 514 and 658 nm."

The different cavity lengths are due to physical size constraints.

10. P5L14-15: See comment 5.

We have reworded the following in the manuscript (P6L8-10) so that it now

reads:

"Extinction coefficients were converted to ensemble extinction cross sections (m^2) by dividing by the aerosol number concentrations measured using a CPC (see Sect. 2.4). The ensemble extinction cross section is hereafter referred to as the extinction cross section."

11. P5L20: Were the CRDS cells made of teflon or metal? If they were metal, please specify the material.

We have added the following sentence to the manuscript (P5L17-18):

"The CRDS cells were made of aluminium."

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?

This is a good suggestion. Figure 1 has been modified in the manuscript.

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?

We have reworded the following in the manuscript (P7L7-11):

"For PAS cells in series with the CRDS channels (PAS 4 and PAS 5), the CRDS-measured extinction coefficients were used directly to calibrate the corresponding in-line PAS channel measurements of IA. This calibration relation between sample extinction and IA is quantified at multiple values of ozone concentration, controlled by varying the discharge frequency on the coronal ozone generator."

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?

The flow was a mixture of pure oxygen (the ozone generator was not powered at

this point) at a flow rate 0.02 L min^{-1} and filtered air at a flow rate of 0.98 L min^{-1}. The filtered air flow was filtered using a particle-filter. Hence the following has been modified in the manuscript (P8L1-4):

"At the start of each calibration cycle, pure oxygen was introduced into the PAS cells through the ozone manifold at a flow rate of 0.02 L min^{-1} per cell, in addition to the 0.98 L min^{-1} filtered-air flow. Air was filtered using a particle filter (Headline Filters, DIF-LK40). The oxygen displaced a fraction of the filtered-air flow through each cell, changing the gas composition, speed of sound and thus cell resonant frequency, as shown in Fig. 2."

15. P6L20: "The 515 nm PAS cell. . . " Isn't the wavelength 514 nm?

Yes, the wavelength is 514 nm. We have reworded the following sentence in the manuscript (P8L9-10):

"The 514 nm PAS cell was calibrated using the 658 nm CRDS cell, and hence the ozone splitting ratio between PAS cells 3 and 4 was used."

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, Δν, calculated from Eq. 2 was between 2 and 28%?

To clarify this point, lines P8L10-14 has been changed to:

"The ozone splitting ratio represents the fractional difference in the ozone concentrations within two PAS cells due to unequal flow splitting within the ozone manifold. The ozone splitting ratios, and therefore the ozone-laden flow rates, between two PAS cells located in parallel (for example, the PAS 2 and PAS 4 cells) were in the range 2–28 %. Measuring the ozone splitting between PAS cells using the resonant shift method compared extremely well to in-line mass flow measurements."

17. P7L7-9 and P8 Figure 3: "Ozone concentrations in the range ~10-500 ppm were used." How did you determine the ozone concentrations? Figure 3 shows a maximum extinction of 27 Mm^{-1} at 405 nm. If this is only from ozone, this gives an ozone concentration of ~660-750 ppmv (σ_{ozone} around 405 nm is 1.45 – 1.65 × 10^{-23} 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 ~50 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?

We have updated the precision of the ozone concentrations, calculating them by dividing the extinction coefficient by the ozone absorption cross section at a wavelength of 405.03 nm and assuming 2.46×10^{25} molecules of air per cubic metre at the 405 nm CRDS cell temperature and pressure of 21.82 °C and 1001 mb. The following paragraph in the manuscript has been modified (P8L22-P911):

"Calibrations involved the stepwise measurement of nine ozone concentration levels, where Fig. 3 shows the PAS and CRDS responses to ozone at 405 nm. Using the minimum and maximum extinction coefficients for ozone in Fig. 3 (1.3 and 27.1 Mm^{-1}, respectively), an ozone absorption cross section of 1.62×10^{-23} cm^2 at the corresponding CRDS wavelength (405.03 nm) and assuming 2.46×10^{25} molecules of air per cubic metre at the 405 nm CRDS cell temperature and pressure of 21.82 °C and 1001 mb, the ozone concentrations were in the range 33–680 ppmv (Serdyuchenko et al., 2014). Approximately the same levels of ozone were used in all cells. The ratios of ozone extinction coefficients measured in the 405 and 658 nm CRDS cells compared well to the ratio of the literature ozone absorption cross sections. After accounting for uneven ozone flow splitting between the cells, the ratio of the measured extinction coefficients at 658 and 405 nm agreed with the literature cross section ratio to within 2.0 %. This excellent agreement provides strong evidence that there were no issues with contamination by absorbing gaseous or aerosol species during ozone calibrations."

18. P7L17 (Eq. 3): Why is the resonant frequency represented by ν in this equation, and F_r in Eq. 2?

The following line in the manuscript has been modified (P9L18, Eq. 3) so that ν has been replaced with F_R.

19. P7L18: How is P_L measured? By the photodiode? Also, what are typical quality factors for your instrument?

The following lines have been added to the manuscript (P9L19-20):

"P_L was measured by the photodiode. PAS cell quality factors were in the range 87–93."

20. P8L1 (and elsewhere): I might consider replacing "gradient" with the

more common “slope,” but this is mostly preference on my part.

We would prefer to maintain our original wording.

21. P8 Figure 3: The y-axis units are inverse megameters (Mm^{-1}), while the units in the text (e.g. P4L23 and P5L9) are inverse meters (m^{-1}). Since Mm^{-1} are the customary units in aerosol work, I would suggest changing the units in the text, but whatever you choose, the units should be consistent.

This is a good point. We have changed all units of absorption and extinction coefficients to Mm^{-1}.

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?

We have added the following to the manuscript (P10L10-14):

“The 658 nm CRDS was used to calibrate the 514 nm PAS channel because it extended over a greater range of extinction coefficients (167–1506 Mm^{-1}) than the 405 nm CRDS (1–27 Mm^{-1}). This ensured that the 514 nm PAS calibration covered a range of absorption coefficients greater than that spanned by the nigrosin absorption coefficients. Calibrating the 405 nm channel using the 405 nm CRDS channel, as opposed to the 658 nm channel, would lead to absorption coefficients that were lower by 3.2 %.”

23. P8L17: Please provide the product number and lot number for the nigrosin used.

We have modified the following in the manuscript (P10L21):

“Water-soluble nigrosin, a strong light-absorbing dye at visible wavelengths, (Sigma Aldrich, CAS Number 8005-03-6, lot number MKBR1705V, product number 198285-100G) was dissolved into high purity deionised water (VWR Chemicals) with a range of concentrations between 3.2–7.1 grams per litre (g L^{-1})”

24. P9L2: What was the DMA sheath flow?

We have added the following in the manuscript (P11L6-8):

“Flow rates through the mass flow controller were set to regulate the flow through the DMA such that the sample-to-sheath flow ratio was at least 1:10 with a sample flow rate in the range 0.3-0.4 L min^{-1} and sheath flow rate in the range 3.5-4.0 L min^{-1}.”

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.

We have adjusted Figure 1 (P9L11).

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) 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: 1.01×10^{-12} m^2 at 405 nm; 1.06×10^{-12} m^2 at 514 nm; and 1.10×10^{-12} m^2 at 658 nm. The absorption cross section that I calculate for 400 nm particles at a wavelength of 514 nm (1.69×10^{-13} m^2) is higher than the value shown in Figure 5f ($\sim 1.4 \times 10^{-13}$ 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?

Our apologies, this was due to a plotting inaccuracy where the figure was incorrectly modified to display the absorption cross section, which has now been amended in the manuscript. All other instances in the analysis script are correct and the result of the paper is not impacted.

27. P12L19-20: See comment 5.

We have clarified this point by modifying the following sentence in the manuscript (P15L5-7):

"The ensemble extinction cross sections (hereafter referred to as extinction cross section) for nigrosin with mobility-selected diameters in the range 250–425 nm were measured using CRDS and modelled using Mie theory, as outlined in Sect. 2.5."

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?

They are ensemble cross sections. The labels in Figures 6 and 7 have been modified (P15-16).

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 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.

We have modified the labels in tables S1 and S2 to be consistent with the rest of the manuscript.

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?

In the first instance 'bdry/bdry' refers to one of the 405 nm PAS cells and the 405 nm CRDS cell and the second instance 'btd/bdry' refers to another 405 nm PAS cell and the same 405 nm CRDS cell. One reason for the difference between the gradients for the two PAS cells is due to different microphone sensitivities. However, it is not clear what the reviewer is referring to by 25 % differences in the gradient.

Technical corrections

All the 'et al.' instances have been addressed. The 'M' in 'McManus' has been capitalised in both instances. All missing doi have been added where appropriate.