

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 2

1. P1L10-11: "Photoacoustic instruments require calibration, which is often achieved by measuring the photoacoustic signal generated by known quantities of gaseous ozone." I'm not sure how often ozone is really used to calibrated photoacoustic instruments. Please quantify or replace with "Photoacoustic instruments require calibration, which can be achieved by measuring the photoacoustic signal generated by known quantities of gaseous ozone."

We have modified the following sentence in the manuscript (P1L10-11):

"Photoacoustic instruments require calibration, which can be achieved by measuring the photoacoustic signal generated by known quantities of gaseous ozone."

2. The ozone calibration of photoacoustic instruments for the measurement of aerosol absorption coefficients needs to put into the context of the calibration of such instruments with aerosols and other calibration gases. I recommend adding a short paragraph to the introduction. The following references, in addition to those already in the manuscript, come to mind: (Arnott et al., 2000; Gillis et al., 2010; Nakayama et al., 2015; Tian et al., 2009).

We have added the following to the manuscript (P2L33-P3L3):

"There exist a number of options for calibrating photoacoustic spectrometers including use of nitrogen dioxide (Atnott et al., 2000; Nakayama et al., 2015), polydisperse kerosene soot (Nakayama et al., 2015), oxygen (Tian et al., 2005; Gillis et al., 2010) and ozone (Lack et al. 2006; Lack et al., 2012; Bluvshstein et al., 2017). Ozone was chosen as the calibrant for our PAS cells, in part as nitrogen dioxide has been shown to introduce uncertainty in calibrations at 405 nm due to photolysis (Lack et al., 2012) and generation of aerosol particles is challenging in the field."

3. P4L28: “without the need for instrument calibration”. This is not entirely correct; one needs to calibrate for mirror losses and the effective cavity length needs to be determined especially as the mirrors are purged with clean air.

We have modified the following 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).”

We have also determined the CRDS R_L factor for ozone (please refer to our response to reviewer 1, comment 9).

4. P5L3-4: Please give the radius of curvature of the cavity mirrors.

We have modified the following sentence 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).”

5. P5L13: Please explain how the R_L factors were determined.

The following was 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 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).”

These different R_L factors have been propagated through the analysis (please refer to our response to reviewer 1, comment 9).

6. P5L14-15: Replace “extinction cross sections” with “average extinction cross sections”.

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.”

7. P5L19-20: “Teflon tubing was used throughout the flow system to minimize contamination.”. Add “and reduce ozone losses”. Please also specify the material used for the insides of the CRDS and PAS cells.

We have modified the following sentence in the manuscript (P6L14-15):

“Teflon tubing was used throughout the flow system to minimise contamination and to reduce ozone losses.”

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

“The CRDS cells were manufactured from aluminium.”

The PAS cells were manufactured out of Aluminium. Please refer to P4L12.

8. P8L1-3: Please also discuss the zero-offset of the linear regressions here and elsewhere unless the regressions were forced through zero; if this is the case please note this.

The following sentence has been added to the manuscript (P9L25):

“All regressions relating to the calibrations were forced through zero.”

9. P8L11 Eq. 4: This seems to assume that the wavelength dependence of absorption equals that of extinction. How large is the influence of scattering (Rayleigh plus particle contamination)?

We have added the following to the manuscript (P10L14-18):

“In the calculation of the extinction coefficient (see Eq. 1), the Rayleigh scattering term is common to both the τ and τ_0 measurements and therefore does not contribute to the extinction. Thus it is valid to scale the extinction coefficient measured with the CRDS at 658 nm (or 405 nm) by the literature absorption cross section ratio. What this analysis does not account for is any small difference in the Rayleigh scattering of air versus the Rayleigh scattering of air with a small ozone concentration (up to 680 ppm).”

10. P15L6: “Our result is robust for optical wavelengths between 405 and 658 nm.” This seems to be overstating the results as measurements at

only one wavelength (i.e., 514 nm) between 405 and 658 nm were discussed.

We have modified the following sentence in the manuscript (P17L6):

“Our result is robust for the optical wavelengths 405, 514 and 658 nm.”