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Atmospheric Measurement Techniques
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Interactive comment on "Calibration of a photoacoustic spectrometer cell using light absorbing aerosols. A technical note" *by* Nir Bluvshtein et al.

Anonymous Referee #1

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To reduce uncertainty associated with aerosol impacts on atmospheric radiative transfer and heating, high accuracy measurements of the fundamental absorption properties of atmospheric particles are needed. Photoacoustic spectroscopy (PAS) is increasingly being applied to this problem on account of its potential to offer significantly higher accuracy than traditional techniques. However, the accuracy of the PAS technique depends strongly on the efficacy of its calibration. A common approach used to calibrate aerosol PAS instruments is to use absorption by gaseous ozone. The study of Bluvshtein compares this calibration approach to a new particle-based method. For calibrations at 404nm, it shows disagreement between methods of the order of a factor of 2. These are attributed to problems with the ozone-based approach. Should this result be generally applicable to PAS systems other than that of the authors, it will have wide ranging impact. However, the paper devotes little attention to understanding the causes for the discrepancies. As such, it leaves significant uncertainty regarding the general applicability of the result to other systems, both in terms of the existence of a bias and its potential magnitude. In summary, this is an important and welcome piece of research that is well suited to AMT, however significant effort should be directed towards understanding and justifying the key results before publication.

Specific comments

- The observed result would be consistent with NO2 contamination in the ozone generation line. Ozone absorbs strongly at 404nm and is also readily photolysed. While the optical power in the CRDS will be insufficient to photolyse NO2, this is not the case for the PAS. Photolysis of NO2 contaminants could lead to the PAS under measuring absorption, as observed. Is this occurring here? There are several ways that the authors could explore this e.g. perform calibrations at different PAS laser powers to change the photolysis rate in the PAS cell. Alternatively, a different analytical technique could be used to quantify NO2 concentration in the calibration flow sample stream. If NO2 absorption is important, then this leads to the question of whether the contamination is unique to this setup or a more general issue.

- Related to the above, the authors describe two methods for generation of ozone – a UV lamp and a corona discharge. It is conceivable that NO2 could be generated from N2 impurities in the O2 carrier gas in the corona discharge. However, a pathway for NO2 generation using the UV lamp method is less clear. Are different ozone calibration slopes observed for these two generation methods?

- One difference between the ozone and nigrosin-based calibrations is the dependence of the former on measurements from the CRDS system. There is no evidence provided to validate the CRDS measurements quantitatively. Presumably the authors would justify the particle CRD measurements based on agreement between the PPFA and SRFA

PAS calibration slopes (which used refractive index values derived from the CRDS) and the nigrosin slope (which used refractive index from ellipsometry measurements). However, this does not provide validation of the gaseous ozone measurements. The cavity RL factor for gas vs aerosol sampling may well be different due to ability of O3 to diffuse into the mirror purge volumes more effectively than aerosol. In the limiting case of O3 filling the full cavity length, this would lead to the CRD over measuring ozone by around 19%. What is the RL factor for gas vs aerosol sampling in the current setup and what is its uncertainty?

- On a related theme, what was the CRD mirror purge flow rate used and was a correction for sample dilution applied in calculation of the CRD ozone concentration?

- Previous studies (e.g. Lack, AST, 2006) have compared ozone-calibrated PAS measurements to Mie calculations for nigrosin and shown agreement to better than 5%. Thus the underlying message of the paper is that the O3 calibration issue is wavelength dependent. Do the authors have the means to verify the result of Lack by repeating measurements at 532nm? This would prove unequivocally that the problem at 404nm is not due to any issues specific to this setup.

- The signal magnitude in the photoacoustic instrument depends on the spatial overlap of the absorbing sample, laser beam and eigenmode pressure distribution within the resonator. Although in theory the eigenmode does not extend beyond the resonator into the buffer volumes, in reality it will. Thus, differences between gas phase and particle calibrations could result from different distributions of aerosol vs calibration gas within the buffer volumes (noting that O3 will diffuse more effectively than particles). In this case, the positioning of sample flow ports on the cells could be important. Where were flow ports positioned on the PAS cells used, and in particular were there differences to Lack et al. (2012)?

- The cavity Q factors for the PAS appear to be significantly lower (by a factor of approx 2) than those reported in Lack et al. (2012) for the same resonators at pressures

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around 100kPa. Why is this?

- More detail on the ozone generation system is needed: what flow rates were used and how were flows regulated? What were the plug flow residence times in the gas delivery lines and detection cells? What materials came into contact with the ozone sample? Does changing the flow rate have any impact on the ozone calibration slope? It shouldn't, but such dependency could arise from e.g. changing the timescales for wall loss or changing timescales for production/destruction of contaminant absorbers.

- Where was the CPC positioned during particle calibrations? Presumably after the PAS cell. What were particle losses in the PAS cell and interconnecting tubing? What was the error on the particle count number?

- The authors state that an impactor was used to reduce the concentration of multiply charged particles. How successful was this approach and what was the contribution of multiply charged particles to total absorption in the sample stream? Were larger particles included in Mie calculations used for the nigrosin-based calibrations?

- A lot of technical information is provided regarding the ellipsometry method used to determine the complex refractive index of nigirosin. However, for those unfamiliar with this technique, it is not immediately clear how errors on these measurements are derived. For example, does the structure of the thin layered nigrosin impact its density and refractive index compared to that expected for the bulk. Could this introduce systematic errors in the complex RI determined? Nigrosin density was taken to be 1.6 g cm-3. What is the error on this number and how does it propagate to uncertainty in the complex RI?

- Many of the above questions point to the need for a critical assessment of the errors associated with both the ozone and particle based calibrations. For the latter, the authors need to estimate errors in particle size, size distribution, complex refractive index, number concentrations and propagate these through a Mie routine to see what the impact is on the derived absorption coefficient.

- It is not clear from where the nigrosin used in these studies was sourced. Nigrosin appears to be a complex mixture of components and thus to what extent are its optical properties expected to vary between batches, samples and suppliers? This is important to know if nigrosin is to be adopted widely as a calibration standard.

- Lines 272-280: more information is needed here. How was the system set up in tandem? Was the CRDS sampling before or after the PAS cell (or both) and what flow rates were used? Some quantitative information on results from these tests would be welcome.

Technical corrections

Line 13: reword to avoid starting sentence with ‘And’. This doesn’t read well.

Line 18: change ‘offer’ to ‘offers’

Line 18: change ‘the PAS’ to ‘photoacoustic instruments’ to improve flow.

Line 26: replace ‘to the top’ with ‘at the top’

Line 28: replace ‘clouds’ with ‘cloud’

Line 39: The fact that BC and BrC absorb does not introduce a need to measure absorption. The need is that we need to characterise the absorption properties of BC and BrC with high accuracy to understand impacts on the atmosphere.

Line 70: do the authors mean transmittance measurement here? For example Lack et al compare to CRDS-derived extinction measurements.

Line 76: insert ‘phase’ to read ‘gas phase absorption’

Line 82: correct spelling on ‘photolayses’

Lines 95-100: it would be worth stating explicitly here why particle based cals may be harder to implement in field applications e.g. due to the need for particle generation, size selection and counting equipment.

Line 122: would these notches be better described as buffer volumes?

Line 125: replace ‘at the background’ with ‘in the background’

Line 129: replace ‘were’ with ‘where’

Line 193: correct spelling for nigrosin

Line 224: add the RH to which the samples was dried here

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