

## ***Interactive comment on “Calibration of a photoacoustic spectrometer cell using light absorbing aerosols. A technical note” by Nir Bluvshstein et al.***

**Nir Bluvshstein et al.**

yinon.rudich@weizmann.ac.il

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Anonymous Referee #1

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 Bluvshstein compares this calibration approach to a new particle-based method. For

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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.

Reply: We thank the Reviewer for the careful reading of the manuscript and his/her supportive comment.

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 NO<sub>2</sub> contamination in the ozone generation line. Ozone (did you mean NO<sub>2</sub>?) absorbs strongly at 404nm and is also readily photolysed. While the optical power in the CRDS will be insufficient to photolyse NO<sub>2</sub>, this is not the case for the PAS. Photolysis of NO<sub>2</sub> contaminants could lead to the PAS under measuring absorption, as observed. Is this occurring here?

Reply: NO<sub>2</sub> contamination in the corona discharge ozone generation line is possible if H<sub>2</sub>O and N<sub>2</sub> are available. To avoid this possibility, the dry N<sub>2</sub> (from a liquid N<sub>2</sub>) was mixed with the O<sub>2</sub>/O<sub>3</sub> mixture down flow from the corona discharge instrument. Additionally, ozone was generated by two independent sources, with similar results: a constant flow of high purity (99.999%) O<sub>2</sub> through the UV lamp O<sub>3</sub> generator and a corona discharge ozone generator. These considerations make NO<sub>2</sub> contamination in the corona discharge ozone generation line improbable. We addressed this issue in added remarks in the manuscript section “PAS calibration”.

There are several ways that the authors could explore this e.g. perform calibrations at

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different PAS laser powers to change the photolysis rate in the PAS cell.

Reply: We have performed the O<sub>3</sub> calibration at different instrumental configuration and discuss the results in the context of possible NO<sub>2</sub> contamination in the supplementary material. We concluded that the effect of such contamination if exist at all is negligible in our system.

Alternatively, a different analytical technique could be used to quantify NO<sub>2</sub> concentration in the calibration flow sample stream.

Reply: Following to the above explanation we did not see the need for such measurement.

If NO<sub>2</sub> 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 NO<sub>2</sub> could be generated from N<sub>2</sub> impurities in the O<sub>2</sub> carrier gas in the corona discharge. However, a pathway for NO<sub>2</sub> generation using the UV lamp method is less clear. Are different ozone calibration slopes observed for these two generation methods?

Reply: We show in the supplementary material comparison between different calibration curves performed at different instrumental setup and with using the two O<sub>3</sub> generation methods on the same day. Results shows that the calibration slopes differ by less than 5%.

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).

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However, this does not provide validation of the gaseous ozone measurements.

Reply: We added a supplementary material section which describes validation of the CRD-S response and data analysis using both gas (N<sub>2</sub>) and aerosol filled cavity.

The cavity RL factor for gas vs aerosol sampling may well be different due to ability of O<sub>3</sub> to diffuse into the mirror purge volumes more effectively than aerosol. In the limiting case of O<sub>3</sub> 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?

Reply: RL factor calculated from the cavity geometry is  $1.187(\pm 0.003)$ . The RL factor was additionally calculated by measuring the CRD-S response to 90% N<sub>2</sub> 10% O<sub>2</sub>/O<sub>3</sub> mixture in a center inlet and side outlets configuration with and without purge flows. The difference between the two calculated values was below 1%. We acknowledged that with side inlet and side outlet CRD-S configuration, the uncertainty in RL may lead to substantial errors in aerosol measurements. For this reason we do not use this CRD-S configuration.

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?

Reply: The CRD-S purge flows in our system are about 40 cm<sup>3</sup>min<sup>-1</sup> each and dilution correction is not needed because of the center-inlet CRD-S configuration as described in the text.

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 O<sub>3</sub> 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.

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Reply: Currently a 532 nm PA-CRD-S system is not available and we do not have the ability to perform such validation. Still, for measurements of absorption in short wavelengths this may pose a problem

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 O<sub>3</sub> 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)?

Reply: The PAS cell used in this study is similar to the one described by Lack et al. (2012) and to other instruments used in reported literature (see text for references). We agree with the referee in regards to the potential importance of gas Vs. aerosols diffusion and spatial distribution inside the PAS cell. Unfortunately, we do not have the means to test whether or not this is the cause for the ozone and nigrosin calibration slope discrepancy.

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 around 100kPa. Why is this?

Reply: In our instrument at about 100 kPa and 296 C with synthetic air in the cell the Fr is about 1363 Hz and the FWHM is about 35 Hz leading to Q of 39. Extrapolating from Lack et al. (2012) their cell would have Fr of about 1360Hz and FWHM of about 15 Hz leading to Q of about 90. It seems that the source for difference in Q is in the FWHM parameter ( $Q/Fr=1/FWHM$ ). We don't have an explanation for this difference but notice that higher value of FWHM means less Fr sensitivity to changes in cell pressure and a

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more stable system.

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?

Reply: We have provided additional details regarding ozone generation and flow conditions.

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.

Reply: Changing the gas flow rate does not change the calibration slope. We pre-formed O<sub>3</sub> calibration using the corona discharge generator in a tandem "PAS first" configuration at flow rates of 100, 300, 600, 900 cc min<sup>-1</sup> with calibration slopes of  $3.967 \times 10^{-7}$ ,  $4.047 \times 10^{-7}$ ,  $3.985 \times 10^{-7}$ ,  $4.020 \times 10^{-7}$  cm<sup>-1</sup> V<sup>-1</sup> respectively.

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?

Reply: Additional details of measurement setup flow and tubing was added to the text. Lack et al. (2012) reported less than 1.5% particle loss for sub-micron particles at 1 LPM flow through the PAS cell and inlet tubing. Particle loss was treated as negligible and was not accounted for in these measurements. Errors on particle count number were taken as the standard error on a 120 seconds 1 Hz data set.

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?

Reply: Additional details regarding the use of the impactor to reduce the effect of mul-

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tively charged particles is provided in the supplementary information. At the nigrosin calibration example given in the main text, multiply charged particles are not included in the Mie routine calculation. However, for the additional analysis presented in figure 5 for SRFA and PPFA, the impactor was not used and the contribution due to multiply charged particles was accounted for both in the complex RI retrieval from CRD-S measurements and in the absorption coefficients that are calculated and presented in figure 5. The agreement between the slope calculated from nigrosin calibration data points and the additional SRFA and PPFA data points implies that the multiply charged particle removal using the impactor worked as well as the multiply charged particles correction used for complex RI retrieval 1-3.

A lot of technical information is provided regarding the ellipsometry method used to determine the complex refractive index of nigrosin. 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?

Reply: The uncertainty analysis of the SE measurements is described in details in the methodology section. An additional analysis was added to the results section regarding possible effects that air voids may have on the retrieval of the complex RI.

Nigrosin density was taken to be 1.6 g cm<sup>-3</sup>. What is the error on this number and how does it propagate to uncertainty in the complex RI?

Reply: Nigrosin density of 1.6 gr cm<sup>-3</sup> was taken from Moteki et al. 4 where it is reported without uncertainty. However the experimental setup used in this paper (DMA-APM; differential mobility analyzer coupled to an aerosol particle mass analyzer) was reported in McMurry et al. 5 with an average uncertainty of 5%. This was used to re-calculate the range of imaginary part of the complex RI of nigrosin from the UV-Vis absorption measurements of diluted aqueous solution.

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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.

Reply: The uncertainties of the complex refractive index retrieved from the ellipsometer measurement and the precision of the number concentration (as standard error of 120 continuous samples) were propagated through the Mie routine as described in the text. The uncertainties on the size distribution was added to the analysis. Table 1 lists all components of uncertainty propagated through the Mie routine.

It is not clear from where the nigrosin used in these studies was sourced.

Reply: Nigrosin was purchased from Sigma-Aldrich (batch number: 14828BD). This information was added in the text.

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.

Reply: Unfortunately, this is a question neither I, nor the supplier (Sigma-Aldrich) can answer. In order to test this issue, I would recommend future users to measure absorption of diluted aqueous solutions and compare calculated imaginary part to results reported in the manuscript or perform ellipsometer measurements using their stock material.

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.

Reply: Additional information regarding the tandem and parallel system configurations

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was added to the main text and quantitative comparison between the different configurations is now presented in the supplementary information.

Technical corrections:

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

Reply: Was rephrased

Line 18: change 'offer' to 'offers'

Reply: Was rephrased

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

Reply: Was rephrased

Line 26: replace 'to the top' with 'at the top'

Reply: Was rephrased

Line 28: replace 'clouds' with 'cloud'

Reply: Was rephrased

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.

Reply: Thank you. The text was modified: "Light absorption properties of BrC and its mixing with absorbing and non-absorbing aerosol components introduce a need for sensitive and accurate direct measurement of light absorbing aerosols which is still very challenging." Was rephrased to: "Light absorption properties of BrC and its mixing with absorbing and non-absorbing aerosol components introduce a need for sensitive and accurate measurements of light absorbing aerosols in order to improve our understanding of the impacts of absorbing aerosols on climate."

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

Reply: We did mean transmittance. CRD-S extinction measurements are essentially measurements of transmission.

Line 76: insert 'phase' to read 'gas phase absorption'

Reply: Was rephrased

Line 82: correct spelling on 'photolayses'

Reply: Was corrected

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

Reply: The sentence was rephrased to: "An alternative calibration method is to use a standard aerosol with well-known absorption properties. PAS calibration using size selected light absorbing particles requires a standard material with accurate information of its complex refractive index at the instrument's wavelength, which is not widely available. This procedure is also time consuming in comparison to the use of a light absorbing gas and may be more difficult to implement on field and aircraft applications due to the need for aerosols generation and size selection equipment."

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

Reply: The two buffer volumes act as acoustic notch filters to reduce acoustic noise at the cell resonant frequency. The term acoustic notches was used by Lack et al. 6 to describe this instrument.

Line 125: replace 'at the background' with 'in the background'

Reply: Was rephrased

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Line 129: replace 'were' with 'where'

Reply: Was corrected

Line 193: correct spelling for nigrosin

Reply: Was corrected

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

Reply: (RH < 10%) was added in the text

Please also note the supplement to this comment:

<http://www.atmos-meas-tech-discuss.net/amt-2016-323/amt-2016-323-AC1-supplement.pdf>

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Interactive comment on Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2016-323, 2016.