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Discussions

Interactive comment on "Development of a cavity enhanced aerosol albedometer" *by* W. Zhao et al.

Anonymous Referee #2

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Cavity ringdown (CRD) and cavity enhanced (CE) spectroscopy are established techniques for measuring aerosol optical properties. Some of these instruments use broadband light sources to acquire the sample's extinction spectrum, thus enabling the aerosol extinction to be separated from structured gas phase absorptions (in this case from NO2). Here the authors combine a CE system with an integrating sphere (IS) to additionally access aerosol scattering measurements – although this has been done before in single-wavelength cavity systems, to my knowledge this work is the first to incorporate an IS into a broadband CE system. The authors have tested their instrument in the lab using size-selected polystyrene aerosol; they also show some convincing examples of ambient aerosol and NO2 measurements which they compare with commercial instruments. The instrument development aspects of the work have been done well. There are deficiencies in other aspects, however, which need to be addressed before the work is suitable for publication: not placing the work into the wider scientific

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context [1] nor appropriately citing other previous work [3,17,24,27,32], inadequate or ambiguous explanation about how the authors did the work or drew their conclusions from the data [2,4,5,6,7,8,28,33,36], and English language issues [9].

Comments

[1] The authors need to do more to place their work into context. The Introduction would benefit from a brief discussion of the atmospheric and climate relevance of aerosol scattering versus absorption, and hence establish why it is desirable to have an instrument that can quantify both these aerosol optical properties. This scene-setting information needs to come before the otherwise good &thorough review of existing instrumentation. At the other end of the paper, the Conclusions section should include examples of how the authors propose this new instrument could be applied to make atmospheric measurements, to address current uncertainties etc.

[2] Definitions of the terms involved in the key equation 1 on page 2989 were inadequate. Hence how the authors apply equation 1 for their measurements is unclear. The total extinction coefficient of an atmospheric sample is the sum of aerosol extinction, gas absorption and Rayleigh scattering by the gas: alpha_total = alpha_aerosol_ext + alpha_gas + alpha_Rayleigh. However if, as here, both the I(lambda) and reference I_0(lambda) spectra are obtained in air, Rayleigh scattering is present in both spectra, and cancels. Consequently the measured absorption (alpha_meas = alpha_aerosol_ext + alpha_gas) is equal to the lower line of equation 1 but without the alpha_Rayleigh term. The measured extinction coefficient (alpha_meas) is also smaller than the gas sample's total extinction (alpha_total) by the amount equal to the Rayleigh extinction of air, due to the way the I_0 reference spectrum was acquired. For this reason Washenfelder et al (2013) added a Rayleigh term for N2 back into their version of equation 1 (their I_0 reference gas was N2). Conversely, when the I(lambda) and reference I_0(lambda) spectra are obtained in different gases (for example to measure the mirror reflectivity), the relevant quantity is the *difference* in Rayleigh scattering in the two gases, and this could be a positive (e.g. SF6) or a negative (e.g He) quantity,

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see Fig 4b. Much more explanation is required here by the authors.

[3] Page 2989 line 20 to Page 2990 line 5 seems to be an abridged version of text drawn from Section 3.1 of Washenfelder et al, AMT, 6, 861, 2013. This Washenfelder 2013 work is not cited in this section of text; instead the Washenfelder 2008 work that is cited here is a carry-over from the text drawn from Washenfelder 2013. Additionally, the text and analysis approach in 2995 lines 13-25 is rather similar to section 3.3.1 of Washenfelder at al 2013 (which isn't credited on page 2995).

[4] Three of the claims for the instrument's precision and accuracy in Section 3.3 looked optimistic (or at least, they represent very best case scenarios). [a] 2993 line 7 "lowest detection limit of 0.07 Mm-1 (on the scattering channel) with an optimum integration time of 459s". It may be true that these values correspond to the very lowest individual data point around the minimum of the Allan variance plot in Fig 5(b). However the data points are quite scattered here, so the authors should choose values representative of the collection of data points around the minimum. Also, the minimum in the Allan plot for the extinction channel has an integration time of only 54s. So it's not obvious what practical use a 459s (but very sensitive) measure of the scattering would be if there is no equivalent extinction measurement – making both measurements together is one of the selling points of this new instrument. [b] Line 19 "the drift of the LED intensity is not included (in considering the accuracy of the extinction measurements)". This is an awkward omission because the Allan plot in Fig 5 says that, to achieve optimal performance, the I_0 reference spectrum should be re-acquired every 54s. Frequently re-recording the I_0 reference severely limits how much time can be devoted to ambient air measurements. Indeed it may be impractical to frequently re-acquire I_0 because it will take time for the N2 flow (or zero air) to flush the cavity. Comment #2 by Reviewer #1 makes a related point. [c] Line 21 "The mean uncertainty in the determined (1-R) was less than 1%". I don't see how the authors can claim the (1-R) measurement's uncertainty is smaller than the uncertainties in the quantities on which this measurement relies. The uncertainties in the Rayleigh cross sections are 1% for

N2 and 3% for SF6 [see 2991 line 8].

[5] 2996 line 8 onwards. It would be preferable if the authors summarised the previous RI measurements on PSL aerosol before they state "our results [delete "were"] agree with. . ." The previous reports cited in the text are for different wavelengths from 470nm used here. So establishing the agreement requires some interpolation – I would like to see a plot showing the real and imaginary parts of RI versus wavelength from the previous reports and this paper's new measurement to illustrate the interpolation process and the resultant agreement. An earlier study from these authors (Zhao et al., Analytical Chem, 2013, which is not referenced in this section of text) found the RI to be 1.625 + i0.038 for PSL between 442-472 nm. The authors should include their earlier measurement in the interpolation plot, and discuss any difference with the present result. (A related minor point from line 14: "interpolation of their data". Whose data? - Nikolov & Ivanov? Should the interpolation not also include all the available data?). Earlier, 2995 line 2 describes PSL as "non-absorbing", yet the previous reports and one of the two fits from this work show RI has a small absorbing part. Are we now reaching consensus that PSL absorbs weakly?

[6] 2998 line 4 onwards and Fig 9. The logic behind trying two different wavelength windows to retrieve NO2 concentrations was not explained; the conclusions to be drawn from Fig 9 weren't explained either. The DOAS literature contains many investigations into establishing the optimum wavelength window for retrieving molecular absorption signals; there are analogous tests for broadband CE systems, for example, Chapter 3 of "Cavity Ring-down Spectroscopy: Techniques and Applications", Berden & Engeln (editors) Wiley 2009. The net result is that NO2 concentrations retrieved from long and short fitting windows ought to be the same (although the uncertainty on the fitted NO2 concentration will change depending on the data quality included in the fitting windows). That different NO2 concentrations were produced in Fig 9(a) suggests an instrumental or spectral fitting issue, potentially with determining the wavelength dependence of the mirror reflectivity, or a subtle change has happened in the LED's output, or the polyno-

mial used in the DOAS fit doesn't completely account for the aerosol's extinction thus generating an interference for NO2. The authors need to be clear about their reasons for showing Fig 9 and the conclusions to be drawn.

[7] 2998 lines 10-20. The TSI nephelometer's 554nm channel was not used to calculate the Angstrom exponent – why not? Surely an extra data point would allow the Angstrom exponent to be better constrained.

[8] 3019 Ambient aerosol Fig 11(a). The albedometer's scattering measurements are consistently higher than the nephelometer if the extinction is large, but are consistently below the nephelometer if the extinction is small – why is this? This effect causes the correlation plot's gradient in Fig 11b (=1.126) to depart from the idea value of 1.00. Actually, the correlation plot looks slightly curved to me.

[9] I agree with Reviewer #1 that, although improved, language issues remain. There are numerous examples of missing "the" or "a", problems with singular versus plural, and missing punctuation. [Some examples: p2983 line 9 "Since [the] aerosol extinction is the sum of [the] absorption and scattering coefficients...". Line 24 "...multiple scattering by [the] filter medium, and [the] angular distribution of [the] scattered light". Line 28 "For... highly light[-]absorbing[,] organic aerosol loading[s], the bias in filter-based light absorption measurement[s] may be larger than 100%." Page 2984 line 13..."such as [the] TSI 3563 integrating nephelometer...". Lines 15-20 "underestimation of scattering coefficient[s]... scattering measurement[s] using a nephelometer... Correction factor[s] for the truncation errors..."]. The authors sometimes form a sentence's subject by grouping several nouns together, and this makes the sentence's meaning unclear or ambiguous. [For example 2984 line 28: "Optical extinction cell approach, limited by the detection sensitivity, is of practical use only in...." would read better as "Optical extinction measurements made in [single pass?] cells are limited by the detection sensitivity and are of practical use only in..."]. The errors are too many to expect a reviewer to list them. The manuscript requires comprehensive proof-reading by the authors and, I suggest, careful checking by the editorial office.

Technical comments & corrections:

[10] 2982 line 11: ..."averaged [not integrated] value over a narrow bandwidth".

[11] Line 13: ... "averaged scattering ". Unclear: averaged over what? – the wavelength range stated in the previous sentence?

[12] Line 18: Be clear that the good agreement with RI in previous papers applies to the laboratory tests on PSL in the previous sentence.

[13] Line 23 "aerosol scattering coefficient[s] and NO2 trace [gas] concentration[s]"

[14] 2984 line 8. Move the Langridge et al citation from line 11 to line 8 where it is first referenced. Explain why they concluded that the PAS technique is not well-suited to measurements at high RH.

[15] 2985 line 12 "this method still involves"...

[16] Line 25. Dial reference is 2010, not 2012.

[17] 2986 line 25: use of the single citation to Zhao et al 2013 (wrongly!) implies that Zhao were the first to use DOAS to separate aerosol extinction from extinction by molecular absorbers in a gas sample. Either cite the earlier work from other groups, or delete the Zhoa reference and refer readers back to the works cited a few lines above.

[18] 2987 lines 14,19 & 22 give dimensions in cm units, whereas the dimensions are shown in mm units on Fig 1. Please make consistent.

[19] Line 23. In addition to the 1.5 L min^-1 flow rate, please provide the residence time of the gas sample inside the instrument. This also relates to point #2 raised by Reviewer #1 and my point [4b].

[20] 2988 line 1. "spectral resolution 0.4nm". Is this FWHM? How was it measured? Is this resolution the same over the spectrometer's full 412-487nm range?

[21] 2989 line 1. What is "r"? Where is this defined?

[22] 2990 line 1. R_L is defined here as the ratio of the total length of the cavity to the length of the cavity occupied by the sample. Yet 2991 line 12 states R_L was measured using a 42 ppbv NO2 sample. Which is correct?

[23] Line 6. "Broadband wavelength measurement of extinction coefficient by IBBCEAS provides..." needs re-phrasing.

[24] 2991 line 2. Add Moosmuller et al (Aerosol Sci Tech 2005) to the reference list. This group was one of the first to use Rayleigh scattering in different gases to determine cavity mirror reflectivity.

[25] Line 14. "The aerosol scattering coefficient, alpha_scat, is proportional..." (not the "scattered light intensity").

[26] Line 15. Needs a clear statement about whether the CCD spectrometer used to measure I_trans is the same spectrometer used in the IBBCEAS measurements.

[27] Line 20. The unfortunate positioning of the Strawa 2003 and Thompson 2008 citations at the end of this sentence implies those works impacted only on correcting a minor truncation error. In fact, Strawa et al produced equation 3, and Thompson et al then added the K' term.

[28] 2993 line 6. Explain how the long-term drift value (smaller than 2 Mm-1) was quantified from Fig 5. (Don't presume the reader should do this him/herself).

[29] 2997 line 12-13. Perhaps it's just clumsy phrasing, but "[The] large fit error observed around 475-481nm" is caused by noise in the data, not a problem with the spectral fit.

[30] 2998 line 3 "tolerance of the NOx detection sensitivity (1 ppbv)" – for which instrument?

[31] Line 14 "zero adjusting" – of what?

[32] 2999 line 6 onwards. The authors note that aerosol extinction measurements by

cavity methods require very stable light sources, and that LEDs are therefore a good choice. Either here in the Conclusions section or on 2986 line 16 where they cite Fiedler et al 2003, the authors ought also to cite Ball et al (Chem Phys Lett 2004) who were the first to demonstrate cavity enhanced absorption using an LED light source. The Fiedler work used an arc lamp which, according to this Conclusions section, the authors consider is less favourable than an LED.

[33] 3012 Fig 4. The meanings of the "X offset" and "Y offset" annotations are unclear. How these offsets are used in the analysis needs to be clearly explained in the text. Please check the equation of the best fit line – are the exponents correct?

[34] 3014 Fig 6. It is very difficult to discern the different symbol shapes in panel (a). Also check the value of the best fit line's intercept = 4.23×10^{-9} Mm^{-1} doesn't look right.

[35] 3015 Fig 7. Provide the +/- uncertainties on the fitted NO2 concentration. Also provide the water concentrations from fitting spectra III of each panel.

[36] 3016 Fig 8. Are the relative humidity measurements in panel (a) from a commercial instrument (what type?) or are they measured by IBBCEAS using the fitted water absorptions (in Fig 7)? Which wavelength window was used for the NO2 retrievals in panel (b)? There is a lot of scatter in the SSA data points, presumably because the integration time of the measurement is quite short – these data will probably look better if they are shown as averages over a longer integration time. Are SSA values around 0.9 reasonable for ambient aerosol? The figure caption attributes differences between the scattering measured by the albedometer and the TSI instrument to larger truncation errors in the TSI instrument. This work has calculated truncation losses for the albedometer and the losses are presumably known for the TSI instrument from its manufacturer – does correction of the two datasets (Fig 8c) for their truncation losses bring them into closer agreement?

Interactive comment on Atmos. Meas. Tech. Discuss., 7, 2981, 2014.