Interactive comment on "Determination of the refractive index of insoluble organic extracts from atmospheric aerosol over the visible wavelength range using optical tweezers" ***by*** Rosalie H. Shepherd et al. Anonymous Referee #3

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Review of Shepherd et al., 'Determination of the refractive index of insoluble organic extracts from atmospheric aerosol over the visible wavelength range using optical tweezers'.
In this manuscript, the authors present measurements of the complex refractive index of insoluble ambient aerosol matter collected on filters from a range of different environments. Refractive index (RI) measurements were made using a combination of optical trapping, white light spectroscopy and UV-VIS spectroscopy. The retrieved refractive index values were then used to model the effect of core-shell particles coated with the organic matter on the aerosol radiative effect.
The reported research is original and well presented, and is suitable for publication

Thank you,

subject to the corrections/clarifications listed below being addressed:
1) Given that the paper looks at extracting the complex refractive index from optically trapped droplets using Mie theory, the authors should be aware of the following refer- ence and include it in the introduction.
R.E.H. Miles, J.S. Walker, D.R. Burnham and J.P. Reid, 'Retrieval of the Complex Refractive Index of Aerosol Droplets from Optical Tweezers Measurements', Physical Chemistry Chemical Physics 14 (2012) 3037–3047.

The following references have been added:-

R.E.H. Miles, J.S. Walker, D.R. Burnham and J.P. Reid, 'Retrieval of the Complex Refractive Index of Aerosol Droplets from Optical Tweezers Measurements', Physical Chemistry Chemical Physics 14 (2012) 3037–3047.

H.-B. Lin, J.D. Eversole, A.J. Campillo, "Identification of morphology dependent resonances in stimulated Raman scattering from microdroplets", Optics Communications, 77(5,6), (1990) 407-410

With the following text added to the paper:

"The use of morphological dependent resonances in Raman Spectra to determine refractive index at a fixed wavelength has been reported by Lin et al. (1990) and references therein and Miles et al. (2012)."

2) Page 3, Line 8-9.

The authors state that 'The technique allowed the refractive index to be resolved to within 0.015 over a large wavelength range of 460 to 700 nm'. I take this sentence to mean that the uncertainty in the RI values extracted using this technique is +/- 0.015. However, in Table 1 much reduced uncertainties are given for the samples tested, which correspond instead to the standard deviation in RI values retrieved from multiple droplets. For some of the samples, no uncertainty is given at all. If the precision of the RI measurement is indeed +/- 0.015 as stated in the introduction (and again on page 10, line 22), then this is the error which should be included in Table 1.

The text in the caption for table 1 has been edited to be clearer:-

"Where more than one particle was analyzed for a single type of sample, e.g. urban spring, the average and standard deviation of the Cauchy coefficients and real refractive index were reported for the particle studied. The standard deviation does not reflect the uncertainty estimated from the fitting process (which is ±0.015 for the real refractive index) but a spread of values obtained for the few particles studied. The range in particle sizes studied is also reported."

The distinction is important as the purpose of table 1 is to demonstrate the number of experiments that were performed (as demonstrated by the first line of the caption "Table described the number of aerosols studied, their determined...") and the range of values measured. The

3) Page 6, Line 2-4.
The authors state that 'The values of the three empirical constants and the radius of the trapped aerosol were iterated until a good comparison was achieved between the simulated and the experimentally obtained Mie spectrum'
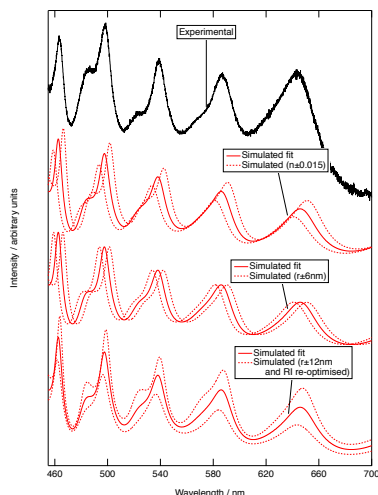Were the experimental and simulated spectra compared by eye or was a fitting algorithm used?

The following text has been added:-

"Typically, the radius of droplet was fixed and the values of A, B, and C varied until a good fit between measured and simulated Mie spectra was achieved by simple comparison (inspection) of peak, trough and inflection point positions. The value of the radius was then iterated through a series of radii with optimization of the values of A, B. and C as a function of wavelength repeated at each radius. Thus, a qualitative grid search was performed over parameter space. Parameter space was A varying from 1.3 to 1.7, B from 0 to 20,000 nm^{-2} and C from 0 to 1×10^9 nm^4. The value of the radius was between 0 to 3 microns typically. The imaginary component of the refractive index was varied only after the grid search for the woodsmoke and humic acid samples shown in fig. 2."

The authors should include a figure which shows how sensitive the simulated spectra are to small changes in the radius and RI, in particular for the more featureless spectra, so the reader can see for themselves the sensitivity of the fit.

The following text and figures have been added to the paper:-

"The sensitivity of the simulated Mie spectra to the refractive index (±0.015) and radius (±6nm) of the droplet are shown in figure 5. The simulated spectra, with the stated variations and the experimental Mie spectra for the Spring Urban aerosol extract are plotted. Figure 5 also contains a third simulated set of Mie spectra calculated by re-optimizing the values of A, B, and C in the Cauchy equation to achieve a fit between simulated and experimental Mie spectra for particles with a radius ±12 nm from the optimum fit to the experimental data. Figure 5 demonstrates that the quoted uncertainties in radius (±6nm) and refractive index (±0.015) are realistic."

(New)"Figure 5: The experimental Mie spectra for the urban spring aerosol extract with the simulated best fit perturbed in three different scenarios to demonstrate the sensitivity of fitting simulated Mie spectra to experimental Mie spectra. Initially the simulated fit (red solid line) is recalculated with a refractive index increased and decreased by 0.015 (n±0.015), followed by the simulated fit (red solid line) recalculated with a radius increased and decreased by 6nm (n±6nm). The final set of simulated Mie spectra consider the simulated fit (red solid line) is recalculated with a droplet radius increased and decreased by 12nm, but the refractive index re-optimized to get the best fit to the experimental fit (r±12nm and RI re-optimized). A clear demonstration that the quoted uncertainties in radius (±6nm) and refractive index (±0.015) are conservative and more than adequate."

4) Page 6, Line 21-22.
The authors should state what the instrument detection limit of the UV-VIS spectrometer was in order to provide an upper bound on the absorbance of the atmospheric samples.

The baseline flatness of Perkin Elmer lambda 950 is quoted as ±0.0008A with a photometric reproducibility of 0.00016A and a RMS photometric noise of 0.0002A. The following text has been added

"The quoted photometric noise for the UV-Vis spectrometer was ~0.0002A. However, the urban and remote aerosol extracts were diluted in isopropanol to fill the UV-Vis spectrometer cuvette and thus a value three orders of magnitude larger than ~0.0002A may provide an upper bound for the absorbance of the samples reported below the detection limit."

5) Figure 7
In keeping with the description in the text (Equation 4) the y-axis label should be ARE(TOT). Based on the description of the x-variable as the volume fraction of the shell (page 11, lines 2-3) the x-axis label also needs changing to Vshell/(Vshell+Vcore).

The x-axis has been fixed.

6) There are several places in the text which seem to contradict each other as to how the Angstrom exponent was determined ie. from optical trapping or from UV-VIS spectroscopy, or from both. Please could the authors clarify the following explicitly: Were values of the Angstrom exponent extracted from the Mie spectra and from the UV-VIS spectra independently and these values then compared to show they were equivalent? The authors should include somewhere the values of the Angstrom exponent determined from each method, along with associated uncertainties.

The Angstrom exponent was determined from the measurement of the absorbance of an aerosol sample in isopropanol using a UV-Vis spectrometer. The value of Angstrom exponent was then adjusted (converted) for use with the imaginary refractive index as described in the appendix. The simulated Mie Spectra in Fig.2 were then calculated with and without an Angstrom component to demonstrate that the attenuation of the Mie Resonances (especially at the shorter wavelengths) was consistent with the measured Mie spectra (in figure2). The following text has been added:-

"The Angstrom coefficient determined for the Absorbance in isopropanol or water was adjusted for use with the imaginary refractive index Angstrom relationship (see Appendix). Simulated Mie spectra of wood smoke aerosol and humic acid aerosol were then calculated with and without an Angstrom exponent

absorption to demonstrate that the attenuation in Mie resonance intensity was consistent with absorption as shown in figure 2."

and

"The simulated Mie spectra in Fig 2. were calculated with and without absorption described by an Angstrom exponent to demonstrate that the attenuation of Mie resonances (especially at shorter wavelengths) was consistent with measured Mie spectra."

and

"In a UV-Vis spectrometer the absorption coefficient, β, can be related to the Absorbance, Abs, by,

$$Abs = -\beta l \qquad (3)$$

where l is the pathlength (1 cm for the work described here) and absorbance, Abs has been corrected from base 10 to base e (Petty 2006). The absorption coefficient can be related to the imaginary refractive index, $k(\lambda)$, by

$$k(\lambda) = \frac{\lambda \beta}{4\pi} \qquad (4)$$

as described by Petty (2006). Substitution of equation (4) into equation (3) and subsequently equation (2) demonstrates that the Ångström relationship for absorbance (equation 2) is modified to

$$\frac{k}{k_0} = \left(\frac{\lambda}{\lambda_0}\right)^{-(\alpha-1)} \qquad (5)$$

for describing the imaginary refractive index (see appendix). In essence the value of Ångström exponent, α, measured by the UV-Vis spectrometer is larger than the corresponding value for the imaginary refractive index. Note for the work described here λ_0=460nm. The values of k_0 and α were measured for dilute solutions of the wood smoke extract in isopropanol and humic acid in water. In the optical trap the trapped droplet of wood smoke extract in isopropanol lost all of the isopropanol solvent to evaporation as expected, leaving pure wood smoke extract. The aqueous humic acid solution lost some water to evaporation, but remained an aqueous and more concentrated, solution. As will be described below the mass density of the woodsmoke extract was measured independently. Thus, for the wood smoke droplet the values of k_0 and Abs_0 were corrected for the mass density of wood smoke extract in the optical trap and the attenuation of the resulting Mie spectrum will be shown to be consistent. For the aqueous humic acid solution, the value of k_0 was determined by fitting the attenuation of the Mie spectrum by inspection, $i.e.$ by changing the value of k_0 until the intensity

attenuation of the simulated and experimental Mie spectra matched, thereby calculating the value of the mass density in the trapped humic acid droplet."

The values and uncertainties for the Angstrom coefficient are reported in a new table 2.

Sample	Mass density / g cm^{-3}	Absorption coefficient, β, at $\lambda_0 = 460$ nm / cm^{-1}	k_0 ($\lambda_0 = 460$ nm)	Abs_0 ($\lambda_0 = 460$ nm)	α
Pure Wood smoke extract B	1.64	3033	0.0111 ± 0.0010	-	9.0 ± 0.1
Wood smoke extract B in isopropanol (Fig. 3 – top pane)	6.60×10^{-5}	0.122	$(4.47\pm0.40)\times10^{-7}$	0.122	9.0 ± 0.1
Aqueous Humic acid (Fig. 3 – top pane)	7.00×10^{-5}	1.513	$(4.214\pm0.38)\times10^{-6}$	0.499	4.2 ± 0.1
Pure Humic acid	1.52	25,000	0.092 ± 0.046	-	4.2 ± 0.1
Optically trapped aqueous Humic acid droplet	0.016	273.2	$(1.00\pm0.50)\times10^{-3}$	-	4.2 ± 0.1