

**Reply to 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 #2**

In this manuscript, Shepherd et al. present an optical trapping technique combined with white light spectroscopy to measure the real and imaginary parts of the refractive index for samples of insoluble material from ambient aerosol samples. They use the data to estimate the effects of organic film-coated particles in the atmosphere revealing significant changes in the top of the atmosphere albedo compared to an assumption of equal sized water droplets. This work is interesting and relevant and should be published once the following minor points are clarified or addressed:

Thank you.

1. In the introduction, references to the work of Reid and coworkers on refractive index measurements should be included.

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. The statement of an “unparalleled level of accuracy” seems too strong given the much greater precision and accuracy achievable using cavity-enhanced Raman scattering in optical tweezers.

The statement has been removed and the text now reads:

“Application of the optical trapping technique was successfully employed to determine the refractive index of aerosol over a wide wavelength range”.

Note the Reviewer's comment on the greater precision and accuracy using the cavity enhanced Raman scattering in optical tweezers is erroneous as both techniques use the same fundamental principles of light scattering from a sphere. The Miles et al. (2012) study is undertaken with ideal samples where greater precision is possible owing to the ability to generate a spectrum with a lot of structure and allowing a precise fit. The samples presented in this work are atmospheric, very limited in amount and supplies were exhausted within a few minutes of nebulization. In our previous studies (Jones et al., 2013), we have achieved similar precisions to the cavity enhanced Raman scattering values.

The accuracy comment is surprising as the accuracy is ultimately based on the resolution of the spectrographs used which are similar here and in the work of Miles et al. (2012).

3. Was all the material extracted during sonication with chloroform and water? What about components that are insoluble in these solvents?

Two extra references (should) have been included:-

1. Folch J., Lees M., Sloane Stanley G. H. 1957. A simple method for the isolation and purification of total lipides from animal tissues. *J. Biol. Chem.* 226: 497-509.
2. Bligh, E. G. & Dyer, W. J. 1959. A rapid method of total lipid extraction and purification. *Can. J. Biochem. Physiol.* 37: 911-917.

And the text now reads:-

“The organic material was extracted from atmospheric aerosol based on techniques adapted from Folch et al(1957) and Bligh and Dyer (1959) and the refractive...”

Only material that was soluble in chloroform was analyzed. Extraction by chloroform is an accepted method to remove insoluble surface active compounds from complex media. The cited reference for this process, Bligh and Dyer has been cited on ~44,000 occasions.

Material that did not dissolve in either chloroform or water remained on the filter material or as solid detritus that was filtered out of the chloroform. The following text has been added:-

“The filter debris with un-extracted material was discarded.”

4. Did the authors observe any artifacts of the sonication process (due to formation of radicals) that indicate further chemistry was occurring and changing the samples? Was this controlled for (i.e. a short duration sonication versus much longer sonication)?

There was no change in chemical properties noted owing to sonication. However checks were performed and the following text has been added:-

“The sonication in the extraction process was not found to change the Langmuir isotherm of atmospheric material at the air-water interface.”

5. Why was the mass concentration of humic acid in the droplets so low? At 30% RH, surely most of the water is lost?

The mass concentration of humic acid in the nebulizing solution was kept “low” to prevent potential aerosol heating. As noted in Miles et al (2012) the local RH of a droplet and that measured by the RH probe are frequently different. However the reviewer’ query has highlighted an error which we have corrected with the following text:-

“The concentration of the trapped humic acid was determined to be  $0.016 \text{ g cm}^{-3}$ . The concentration of the aqueous humic acid droplet had increased by a factor of  $\sim 32$  upon trapping, thus demonstrating that water had evaporated from the droplet during the trapping and aerosol equilibration process.”

6. The x-axis in figure 5 is confusing – as it reads, if the shell and core volumes are equal, this parameters goes to infinity. Please clarify. The y-axis label does not match the text (should it be ARE\_TOT?). Further, in the caption, top, middle and bottom are referenced, but the figure is horizontal.

The x-axis has been fixed.

7. Are the droplets fully spherical in these experiments? What would be the signatures of asphericity and how would this impact the fitting of the data?

The following text has been added

“The liquid droplets are assumed to be perfectly spherical. Mie scattering from droplets experiencing small deformation has been shown<sup>3,4</sup> to result in resonances which shift, broaden and split as the droplet asymmetry increases.”

3. S. Arnold, D. E. Spock and L. M. Folan, Opt. Lett., 1990,15, 1111.

4 G. Schweiger, Opt. Lett., 1990, 15, 156.

The formation of an aspherical liquid droplet trapped in a gaseous environment would be somewhat surprising as the interfacial tension responsible for the spherical shape are in the 10’s of  $\text{mN m}^{-1}$  range and far exceed those exerted by the laser trap.

Also, orientation of a spherical particle in an optical trap is independent of the Mie spectrum recorded and thus a rotating spherical particle will not affect the recorded Mie spectrum. However, the orientation of an aspherical particle will give different Mie Spectra depending on orientation. Thus, an aspherical particle will give a changing Mie spectrum. During our previous work with Mie scattering of aerosol liquid droplets we have not encountered such behavior. We have experienced gross asymmetry during collisions of droplets and solid beads (unpublished) which results in complete loss of resonance behavior. Other tell-tale signs to any asphericity of the trapped particles would be an inability to fit the trapped particle to reasonable values of the Cauchy Coefficient as discussed in the new reference, Miles et al. (2012).