



# Laboratory Measurements of Sea Salt Aerosol Refractive Index



R. Irshad (1), R. G. Grainger (1), R. A. McPheat (2), R. G. Williams (2), D. M. Peters (1) & K. M. Smith (2).

(1) Atmospheric, Oceanic and Planetary Physics, Clarendon Laboratory, University of Oxford, OX1 3PU, UK.

(2) Space Science and Technology Department, Rutherford Appleton Laboratory, Didcot, OX11 0QX, UK.

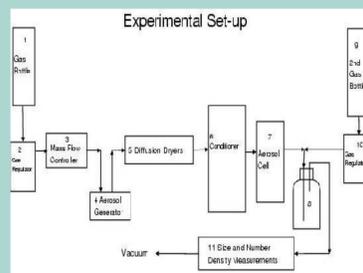
**Introduction** Aerosols play a crucial role in atmospheric reactions and radiative transfer. It is important to understand their properties and behaviour in order to better understand the behaviour of the Earth's atmosphere. Sea salt aerosols provide a significant contribution to the aerosol environment due to the large source area of the oceans, which cover approximately 70% of the Earth's surface.

The optical properties of aerosols are particularly important as they can be used to calculate their direct radiative forcing contribution. Currently, the most commonly used refractive indices of sea salt aerosol are calculated using mixing rules to combine the values for salt and water<sup>1,2</sup>. This is necessary as the composition of sea salt aerosol is determined by the relative humidity which is spatially and temporally variable<sup>3</sup>.

We have measured the extinction spectra of laboratory generated sea salt aerosol from 1  $\mu\text{m}$  to 20  $\mu\text{m}$  using a Bruker 66v/S FT spectrometer. Concomitant measurements included temperature, pressure, relative humidity and the aerosol size distribution. The refractive indices of the sea salt have been determined using a simple harmonic oscillator band model<sup>4</sup> for aerosol with compositions of 0.1-100 % sea salt. The measurements show significant discrepancies when compared to existing sea salt refractive index data.

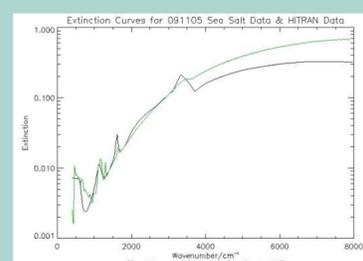
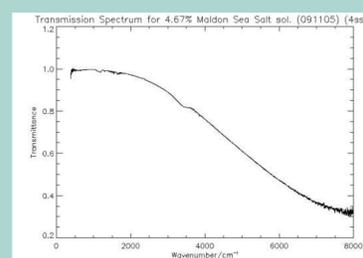
## Experiment

The experiment was set up as shown in the diagram. Sea salt crystals were dissolved in reagent grade water and the solution was nebulised to form an aerosol. This was transported in a buffer flow of  $\text{N}_2$  gas and dried. The aerosol RH was then varied by the introduction of water vapour. The aerosol was carried to a stainless steel cell where intensity measurements were made using a Bruker 66 v/S Fourier transform spectrometer. Finally, the particle size and number density were measured.



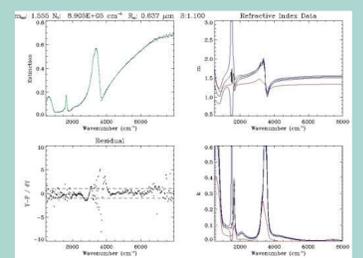
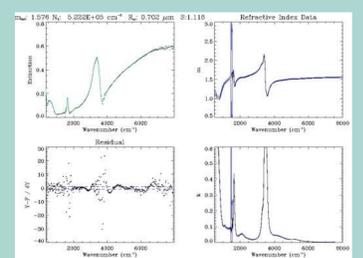
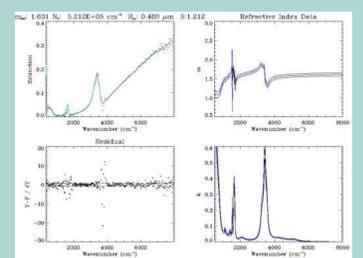
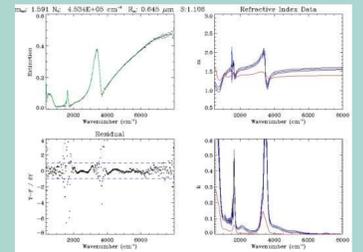
## Refractive Index Retrieval

An example transmission spectrum for sea salt is shown on the top right. Where necessary, gas lines were removed and the refractive index was retrieved using a classical damped harmonic oscillator model<sup>4</sup>. The model provides a best estimate to the shape of absorption bands using a priori data. A Mie scattering algorithm is also used to fully describe the absorption spectra. An extinction spectrum is calculated and fitted to measurements using a numerical optimal estimation algorithm. Extinction plots of HITRAN data (green) and our data (black) are shown on the bottom right.



## Results

The results of the refractive index retrieval are shown to the left. The left-hand plots give the aerosol extinction and fit as well as the corresponding residual values. The right-hand plots show the real (top) and imaginary (bottom) parts of the resulting refractive indices over a range of wavenumbers. The four plots give results for increasing relative humidity values from top to bottom. Where possible, the current refractive index data for the appropriate RH is shown in red over the calculated values.



Refractive index retrieval results for aerosols of RH (from the top down): approx. 92%, 75%, 70% and 61% respectively.

The imaginary parts of the retrieved refractive indices follow the current data quite closely but is generally at a much lower magnitude. However, the real part of the refractive index is consistently of higher magnitude than the current data. The retrieved data also shows significant differences to current data in the region of the O-H stretch associated with water, at  $\sim 3425\text{cm}^{-1}$ . It is suggested that the differences in the size and shape of these and other peaks in the refractive index spectra of current and retrieved data are attributable to the nature of the aerosol solution. As the salt would dissolve in the water, a simple mixing rule is inappropriate for describing the refractive indices.

## Conclusion

It was anticipated that the actual refractive indices of wet sea salt aerosols would differ from current data due to the inadequacy of the volume weighting model for composite aerosols when applied to solutions. Transmission measurements of sea salt aerosols have been made at various relative humidities and particle sizes representative of the lower troposphere. The refractive indices of these aerosols have been retrieved and have been shown to differ from current measurements.

Further work is being undertaken to improve the accuracy of these results by adding more a priori data using measurements of the refractive index in the limit as wavelength tends to zero.

## References

- [1] Volz, F. E. (1972). Infrared refractive index of atmospheric aerosol substances. *Applied Optics* 11(4): 755-759.
- [2] Shettle, E. P. and R. W. Fenn (1979). Models for the aerosols of the lower atmosphere and the effects of humidity variations on their optical properties. *AFGL-TR-79-0214*.
- [3] McInnes, L. M., D. S. Covert, P. K. Quinn and M. S. Germani (1994). Measurements of chlorine depletion and sulphur enrichment in individual sea salt particles collected from the remote marine boundary layer. *Journal of Geophysical Research* 99: 8257-8268.
- [4] Thomas, G. E., S. F. Bass, R. G. Grainger and A. Lambert (2004). Retrieval of Aerosol Refractive Index from Extinction Spectra using a Damped Harmonic Oscillator Band Model. *Applied Optics* 44(7): 1332-1341.
- [5] Rothman, L. S. (2005). The HITRAN 2004 molecular spectroscopic database. *Journal of Quantitative Spectroscopy and Radiative Transfer* 96: 139-204.