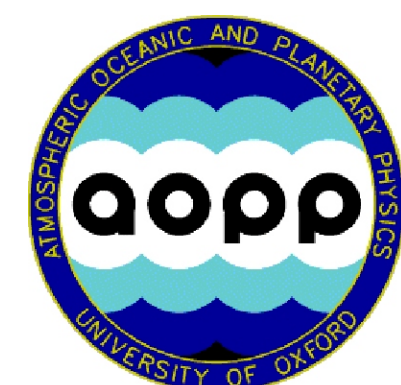




# Verification of a Novel Approach to Laboratory Aerosol Refractive Index Retrieval: Current Status



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**Abstract:** *Aerosols play a crucial role in atmospheric chemical 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.*

*We are currently running an experiment to verify a novel approach to refractive index retrieval from laboratory aerosol absorption measurements. The verification is achieved by dispersing an aerosol with known refractive index (NaCl) and comparing the results with our retrieved values. Sea salt aerosols will also be dispersed - a particularly significant aerosol in climate change because of the large source area. It is anticipated that the data will complement existing measurements of sea salt refractive index.*

*The current status of the experiment is reviewed and the latest results, measured at the Molecular Spectroscopy Facility at the Rutherford Appleton Laboratory, are outlined.*

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## MOTIVATION:

Aerosols have a significant effect on the Earth's radiative balance. They act as cloud condensation nuclei (CCN), affecting cloud albedo [7], and scatter short-wave radiation back into space, thereby reducing visibility and altering climate.

Sea salt aerosol (SSA) particles are particularly important due to the large source area of the oceans. Coarse SSA particles cause corrosion of sensors and stone, and are a main contributor to ocean-atmosphere flux of organic substances, electric charge, micro-organisms, etc. SSA also plays a part in the atmospheric cycles of halogens. For example, SSA is known to react with sulphuric and nitric acids in the atmosphere, releasing HCL gas. [3].

Accurate determination of the radiative effects of aerosols requires a knowledge of aerosol optical properties. Aerosol optical properties are also required for accurate retrievals from satellite instrument data. Current data may be insufficient or, in some cases, inaccurate. Laboratory experiments are required to improve the current knowledge. A new method of retrieving refractive index from transmission spectra has been developed [6]. The molecular absorption of aerosols is modelled using a classical damped harmonic oscillator model which is used in conjunction with a Mie scattering algorithm to fully describe the absorption spectra. This model requires validation. Laboratory experiments are therefore proposed to measure the refractive indices of dry sodium chloride and sea salt aerosols to validate the new retrieval method by comparison with current data.

## 2.3 Aerosol Cell

The MSF small aerosol cell, shown to the right, has an optical path length of 30 cm and an internal diameter of 34 mm. It is a double-walled stainless steel cell with an internal volume of approximately 145 cm<sup>3</sup>.

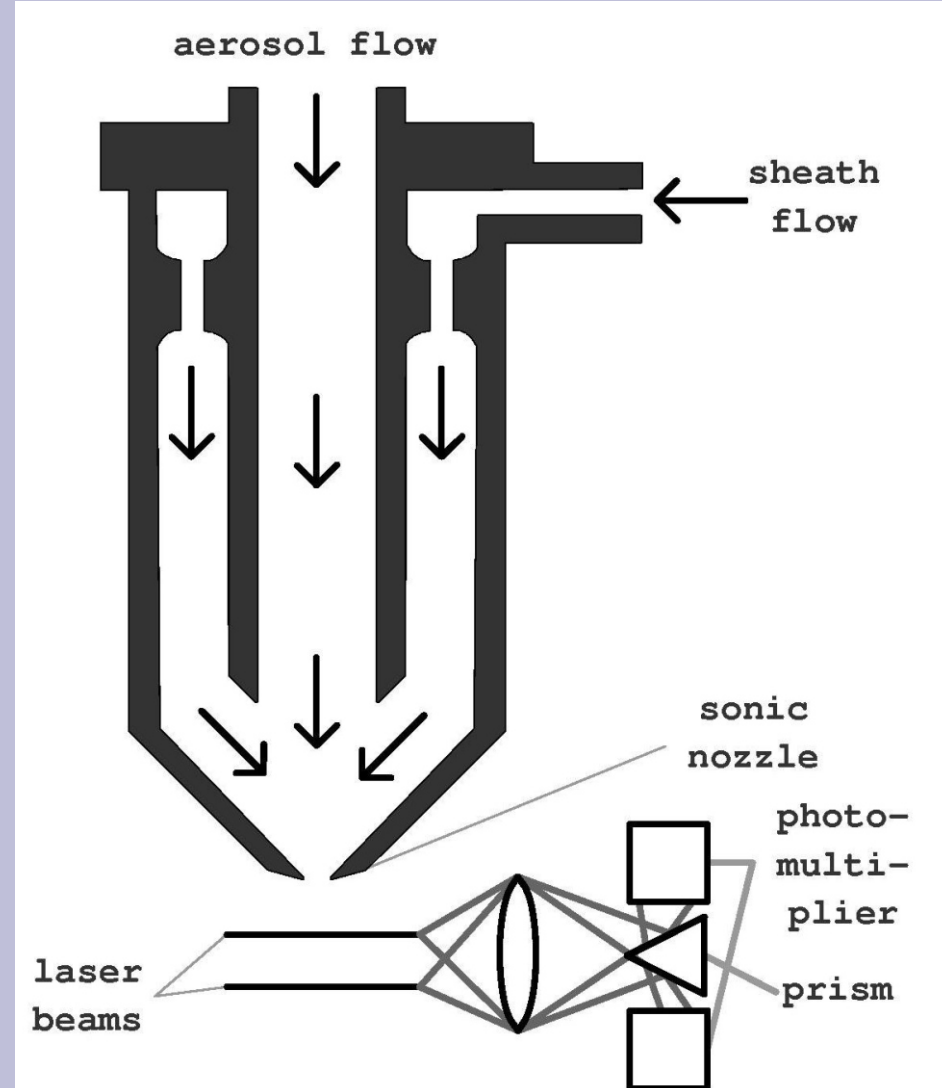


The cell is mounted horizontally inside the evacuated sample compartment of the spectrometer with the beam forming an image point in the middle of the cell. The cell is cleaned before measurements to minimise contaminants.

Spectral measurements are made using a Bruker FTS, as previously outlined. Measurements of the detected intensity are made with and without the presence of aerosol to calculate the actual transmission spectrum,  $T(\lambda)$ .

## 2.4 Particle Size Measurement

The particle size and number density are measured using the Aerosizer LD instrument manufactured by Amherst Process Instruments. An aerodynamic time-of-flight method is used which is independent of refractive index but requires the density of the aerosol sample. It can take both dry powders and wet aerosols and measures particles one at a time in the size range 0.2  $\mu\text{m}$  to 700  $\mu\text{m}$ . Sample times are selected as a series of three minute runs and the instrument can measure up to 10<sup>6</sup> particles per second. A schematic diagram is shown to the right.



The aerosol enters the unit through a capillary tube at the top, as shown. It is then dispersed in sheath air from the outer tubes and accelerated through a nozzle at near sonic velocity to a partially evacuated chamber. The force of acceleration is controlled by the airflow, and smaller particles experience greater acceleration than larger particles. Two laser beams measure the time of flight of the particles as they pass through the measurement region, shortly after passing through the nozzle. The light scattered by the particles is measured by two photomultiplier tubes. The time of flight is defined as that taken for the particles to pass from one laser beam to the next. The start and stop time of each particle are correlated for each size range. The density of the aerosol is entered and used with the time of flight to determine the size distribution of the aerosol (calibration method established by Oskouie et al. [4]).

## 1 Method

The extinction cross-section is required to retrieve refractive index data for aerosols. This is related to the volume extinction coefficient by the following equation:

$$\beta(\lambda) = \int \sigma_{\text{ext}}(r, m, \lambda) n(r) dr$$

Where:

$\beta$  = Volume extinction coefficient.  
 $\sigma_{\text{ext}}$  = Extinction cross-section.  
 $r$  = Particle radii.  
 $m$  = Particle complex refractive index.  
 $\lambda$  = Wavelength.  
 $n(r)dr$  = Number of particles between radii  $r$  and  $r+dr$ .

The volume extinction coefficient is then related to the optical transmission by:

$$T(\lambda) = \exp^{-\beta(\lambda)x}$$

Where:

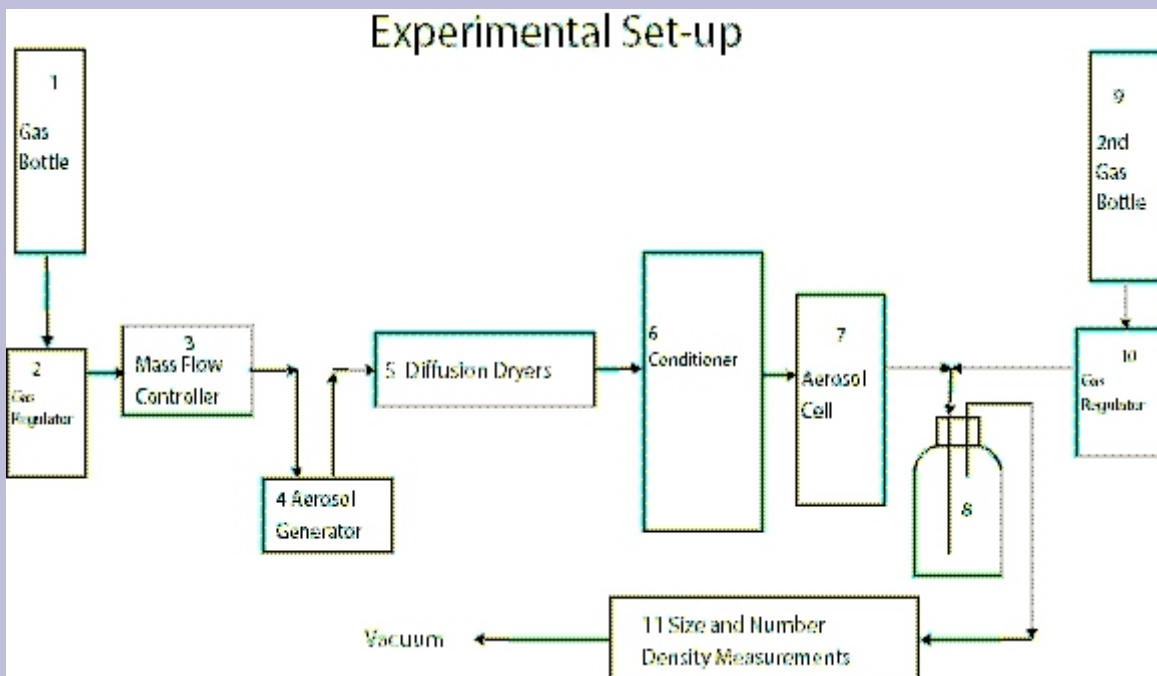
$T$  = Transmission.  
 $\beta$  = Volume extinction coefficient.  
 $x$  = Measurement path length.

Hence to obtain the extinction cross-section,  $\sigma_{\text{ext}}$ , we require measurements of the optical transmission,  $T$ , as well as the particle distribution,  $n(r)dr$ .

## 2 Experimental Set-up

The basic configuration of the experiments undertaken show far is shown on the right. The aerosol is generated by nebulising a solution of the sample in analytical reagent grade water. The resulting hydrated aerosol is then passed through a diffusion dryer to give a dry aerosol sample which is then introduced to the small aerosol cell. Optical windows fitted in the aerosol cell allow measurement of the aerosol absorption using a Bruker IFS 66v/S spectrometer. This is a Fourier Transform Spectrometer (FTS) with moderate resolution (0.12 cm<sup>-1</sup>). All spectra are recorded using a DiATGS detector. The particle size distribution of the aerosol is then determined, as well as the number density, and the aerosol is exhausted into a fume cupboard.

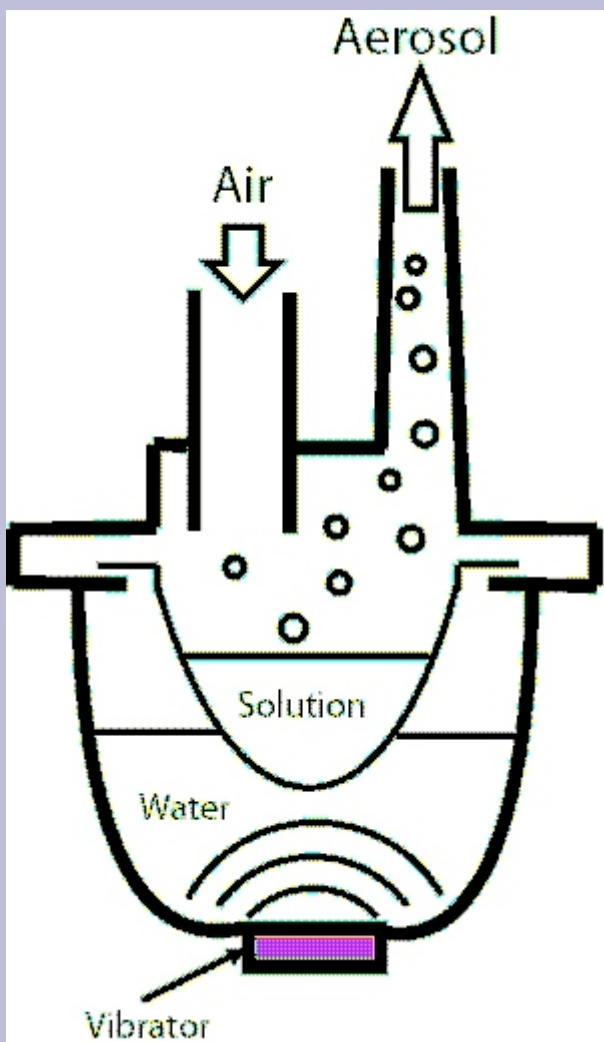
Nitrogen is used as an inert buffer gas and a mass flow controller is used to control the flow to the nebuliser and through to the aerosol cell. The experiments are conducted at room temperature.



## 2.1 Aerosol Generation

The OMRON NE-U17 Ultrasonic medical nebuliser is used to generate liquid aerosol from a solution of salt and analytical reagent grade water. Ultrasonic vibrations are used to nebulise a liquid solution and carry it out of the nebulisation chamber. This is shown clearly in the diagram to the right.

The nebulising chamber consists of a water tank at the bottom of which sits a vibrator. A plastic cup rests in the water and the fluid to be nebulised is placed in this. Ultrasonic vibrations transmitted through the water to the plastic cup cause the liquid to nebulise. Air flow over the nebulisation chamber then carries the aerosol out of the unit. In the experiments undertaken with sea salt and NaCl, nitrogen was used as the buffer gas rather than air.



The unit is able to produce particle number densities of up to 3 x 10<sup>6</sup> pccm, and particles in the size range 1.0 <  $r$  < 8.0  $\mu\text{m}$ , where  $r$  is the particle radius. Once the aerosol is dried, this is equivalent to a size range of 0.1 <  $r$  < 1.0  $\mu\text{m}$ , which is typical of the size range of atmospheric sea salt aerosol in the accumulation mode.

The nebuliser produces a liquid aerosol which must be dried before measurement in the aerosol cell.

## 2.2 Diffusion Dryers

The wet aerosol is dried using two consecutive diffusion dryers [2] shown in the top right hand photograph. A diffusion dryer is a device that removes water from aerosol particles by means of diffusion into beaded silica gel. The aerosol enters the diffusion dryer via stainless steel mesh tubing running through the centre of the device. The dessicating effect of silica gel surrounding the mesh tube causes water to diffuse from the aerosol particles to the silica, where it is absorbed and collected until the silica becomes saturated. The aerosol then passes out of the dryer. The humidity of the output aerosol depends mainly on its residence time in the dryer. The residence time is given by the equation:

$$t = \frac{P(1.33)(273.15)V}{1015Tf}$$

Where:

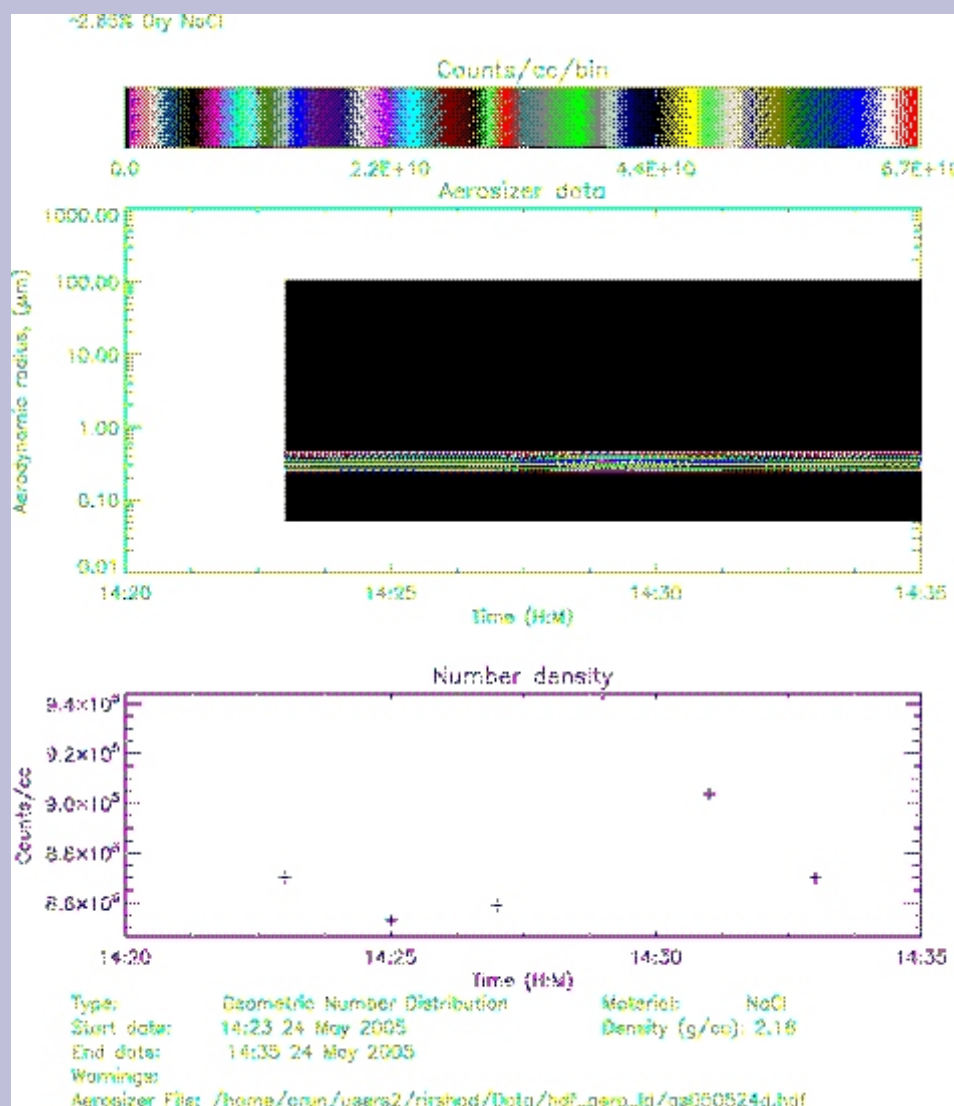
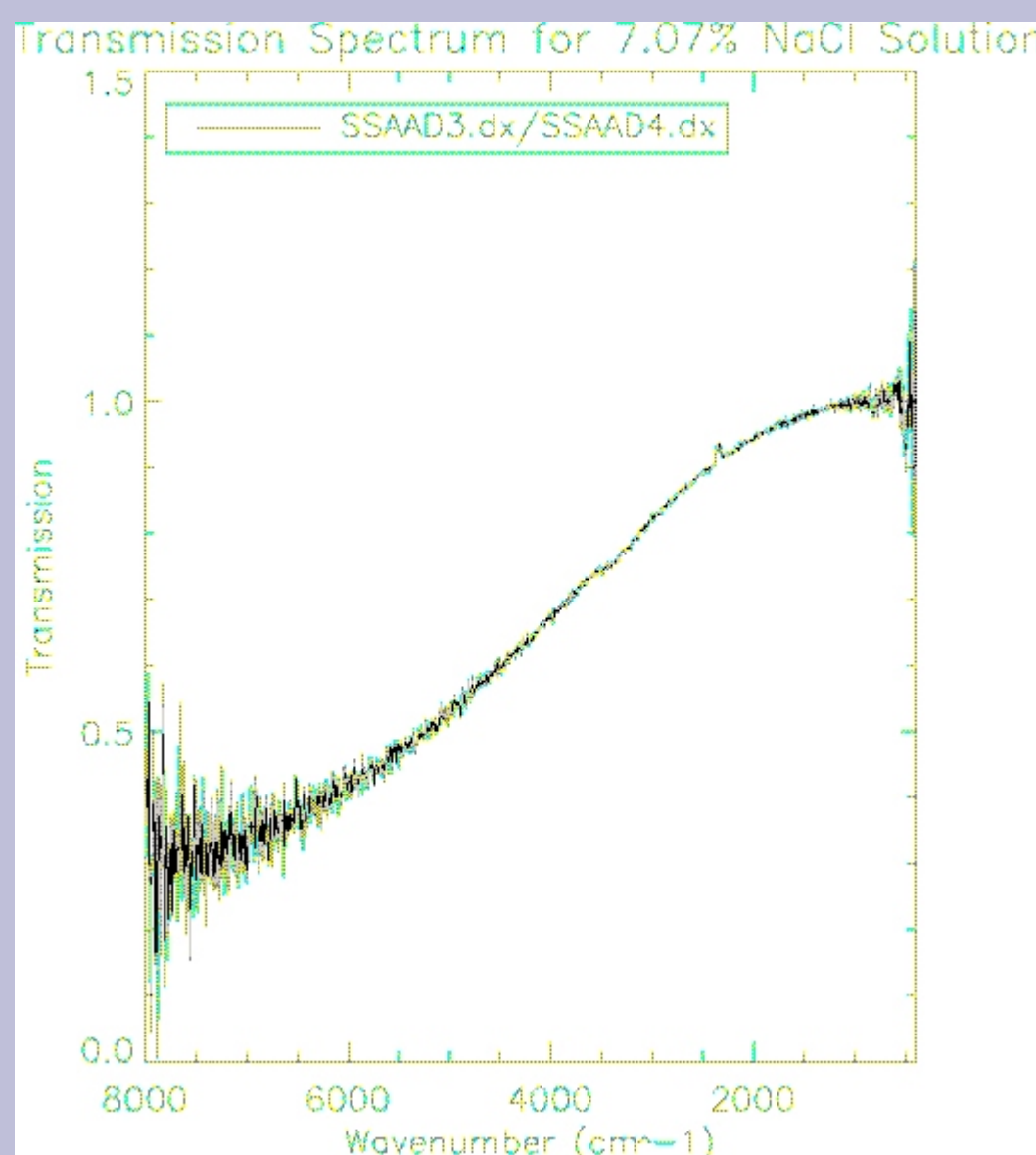
$t$  = Residence time (minutes)  
 $P$  = Pressure (torr)  
 $V$  = Cell volume (cm<sup>3</sup>)  
 $f$  = Flow rate (sccm).

The residence time required for an aerosol to equilibrate to surroundings is of the order of 10 s [1]. Two diffusion dryers of length 40 cm and mesh pipe diameter of 2 cm are therefore used in the course of the experiment to give a minimum residence time of the order of minutes, at a maximum flow rate of 250 sccm. The finished design is shown in the diagram at the bottom right [5].

The dryers are constructed from 10 cm diameter soil pipe with end caps that include o-ring seals and screw caps. Swagelok bulkhead fittings are used to attach the dryers to PFA tubing. The space between the mesh tubing and outer pipe is filled with 2-5 mm orange to green self-indicating beaded silica gel. Small plastic windows fitted in the end caps with solvent cement allow observation of the silica gel during the experiment in order to monitor any colour change. Both dryers are flushed with nitrogen before each use and pressure tested to 1 bar.



## 3 Preliminary Results



Both sodium chloride and sea salt aerosols were successfully produced. Practical difficulties have been encountered with the nebuliser which struggles to disperse solutions with a salt content of greater than 12%. However, the initial concentration of the solution used affects only the dry particle size of the aerosol produced, so this is of little importance. Particle number densities of up to 3 x 10<sup>6</sup> pccm have been obtained.

Further issues with the strength of the laser signal in the spectrometer mean that data obtained during these experiments exhibits a great deal of noise in the transmission spectra. This is due to a misalignment of the mirrors in the FTS and is easily correctable for the next series of measurements. Background spectra are removed from readings using the following relation:

$$\text{Actual Transmittance} = \text{Measured Sample Spectra} / \text{Background Spectra}$$

An example of the transmission spectra obtained for sodium chloride is shown in the above left figure, alongside Aerosizer data on the right hand side showing particle number density and size. While there are certainly absorption features in this spectrum, scattering features are difficult to identify due to the amount of noise in the infra-red. This means that no detailed retrieval of refractive index data may be made from this data set. Spectra obtained from sea salt aerosol also show a similar level of noise in the infra-red, preventing retrieval of refractive index data. However, this is again primarily due to the misalignment of mirrors in the FTS and can easily be rectified for further experimental work. Saturation of the aerosol cell with salt prevented further measurements being taken during these experiments. However, further measurements are planned for October 2005, and it is anticipated that these will provide sufficient data for refractive index retrieval.

## 4 Further Work

Further measurements will be conducted at the RAL MSF in order to obtain transmission spectra of sodium chloride and sea salt with an appropriate signal to noise ratio to allow retrieval of refractive index data. The method described by Thomas [6] will be used to retrieve refractive index from the measured absorption spectra and size distribution..

To allow for measurements of particle size for particles of size less than 0.5  $\mu\text{m}$ , a GRIMM Sequential Mobility Particle Sizer and Classifier instrument will be used. This allows the measurement of particles in the size range 5 nm <  $r$  < 1  $\mu\text{m}$ . It also allows measurement of particle number densities up to approximately 1x10<sup>7</sup> pccm.

Once initial measurements of dry sodium chloride and sea salt aerosol have been completed, further measurements of these aerosols will be undertaken over a range of temperatures and humidities representative of the lower troposphere.

The new retrieval method requires the refractive index at infinite wavelength,  $m_{\infty}$ , (the dielectric constant). This is currently estimated by taking a value of the refractive index from a non-absorbing area of the measured spectra. A direct measurement attempt will be made using the RAL MSF's reflectance spectroscopy accessory on the Bruker IFS 66v/S instrument. This will be achieved by measuring the critical angle in a non-absorbing region of the measured spectra of a bulk sample of sodium chloride and sea salt. This is important to reduce uncertainty in the retrieval method.

## References

- [1] Baron, P. A. And Willeke (2001). *Aerosol Measurement - Principles, Techniques and Applications*. Wiley.
- [2] Thomas, G. E., S. F. Bass, R. G. Grainger and A. Lambert (2004). *Particle Characterization* 4: 112-117.
- [3] Duce, R. A. (1969). On the Source of Gaseous Chlorine in the Marine Atmosphere. *Journal of Geophysical Research* 74: 4597-4599.
- [4] Oskouie, A. K., H. C. Wang, R. Mavliev and K. E. Noll (1998). Calculated Calibration Curves for Particle Size Determination Based on Time of Flight (ToF). *Aerosol Science and Technology* 29: 433-441.
- [5] Temple, J. (2005). Drawings produced by Jonathan Temple, AOPP, Oxford.
- [6] 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.
- [7] Twomey, S. (1960). On the Nature and Origin of Cloud Nuclei. *Bulletin de l'Observatoire du Puy de Dome* 1(1):1-19.