Aerosol optical properties

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ABSTRACT: Traditionally the atmospheric physics department at the University of Oxford has applied optimal estimation techniques for the retrieval of atmospheric properties of gases; temperature, pressure and volume mixing ratio from satellite measurements. This paper describes the latest novel application of these techniques in deriving aerosol optical properties in laboratory experiments. Two examples are given; a spectral resolved technique allows an aerosol refractive index to be derived over a wide wavelength range and a method of deriving single particle refractive index and size from a novel aerosol instrument suitable for in situ aerosol monitoring.

1 OPTIMAL ESTIMATION; A GENERIC METHOD

Optimal estimation has a long history in use in remote sensing. The advantage over other methods is the ability to provide the highest information content for a retrieval problem. This is achieved by using a model that contains all the known physics of the problem and prior knowledge of the measurement. In addition the method provides error estimates on the parameter(s) of interest. The following paragraphs provide a quick overview of the method; for a detailed discussion of the method referrer to Rodgers (2000).

Measurement(s), $\mathbf{y}$ are related to the state, $\mathbf{x}$ by physics. This is represented by the forward model, $\mathbf{F}(\mathbf{x})$. Hence the relationship of the state to measurement can be described by the equation:

$$\mathbf{y} = \mathbf{F}(\mathbf{x}) \tag{1}$$

We need to invert our measurements to find the state, $\mathbf{x}$ (i.e. refractive index, and particle size in the examples to follow). We also use the best knowledge of the solution, $\mathbf{x}_a$ before the measurement was made, thus the problem is to solve the inverse model:

$$\mathbf{x} = \mathbf{F}^{-1}(\mathbf{y}, \mathbf{x}_a) \tag{2}$$

To do this we minimise the cost function Φ, to find the state $\mathbf{x}$:

$$\Phi(\mathbf{x}) = (\mathbf{x} - \mathbf{x}_a)^T \mathbf{S}_{\mathbf{x}_a} (\mathbf{x} - \mathbf{x}_a) + (\mathbf{y} - \mathbf{F}(\mathbf{x}))^T \mathbf{S}_{\mathbf{y}}^{-1} (\mathbf{y} - \mathbf{F}(\mathbf{x})) \tag{3}$$

And we find our estimated state, $\hat{\mathbf{x}}$ is given by:

$$\hat{\mathbf{x}} = \mathbf{x}_a + \mathbf{S}_{\mathbf{x}_a} \mathbf{K}_{\mathbf{x}}^T \mathbf{S}_{\mathbf{y}}^{-1} (\mathbf{y} - \mathbf{F}(\hat{\mathbf{x}})) \tag{4}$$

Where the weighting function $\mathbf{K}_{\mathbf{x}}$ is:

$$\mathbf{K}_{\mathbf{x}} = \frac{\partial \mathbf{F}}{\partial \mathbf{x}}. \tag{5}$$

Equation 4 and 5 are generally by the Levenberg-Marquardt algorithm (Gauss-Newton and the gradient descent iteration methods). For details of how the uncertainty estimates are calculated see Rodgers (2000).

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2 AEROSOL REFRACTIVE INDEX

The following section shows the application of this optimal estimation to determining the spectrally dependent refractive index of aerosols in a test cell.

2.1 *Method*

The extinction cross section of an aerosol in the cell is related to the optical transmission by:

$$T(\lambda) = e^{-\beta(\lambda)x} \tag{6}$$

Where, $T(\lambda)$ is the transmission, $\beta(\lambda)$ the volume extinction coefficient, x path length though the test cell at the wavelength λ. The extinction coefficient can be calculated if we assume Mie theory and know the particle size distribution from the equation:

$$\beta(\lambda) = \int_0^{\infty} \sigma_{ext}(r, m(\lambda), \lambda) n(r) dr \tag{7}$$

Where, σ_{ext} is the extinction coefficient (assuming Mie theory), r is the particle radius, $m(\lambda)$ the refractive index and $n(r)dr$ the number of particles between radii r and $r + dr$.

In this application of the optimal estimation method the forward model $\mathbf{F}(\mathbf{x})$ represents equations 6 and 7, with the state vector, $\mathbf{x}$ containing the size distribution and refractive index. The measurement vector $\mathbf{y}$ contains the spectrally resolved transmission measurement.

Experimental setupFigure outlines the basic configuration of the experiments undertaken. The aerosol is generated (the method is chosen based on the aerosol type) and the aerosol introduced to aerosol test cell. The aerosol cell has optical windows fitted, allowing the aerosol absorption to be measured via the Fourier Transform Spectrometer, FTS. Particle size distribution of the aerosol is then determined using techniques insensitive to particle refractive index and the aerosol vented into a fume cupboard. The configuration also included a water bath to allow the relative humidity to be controlled.

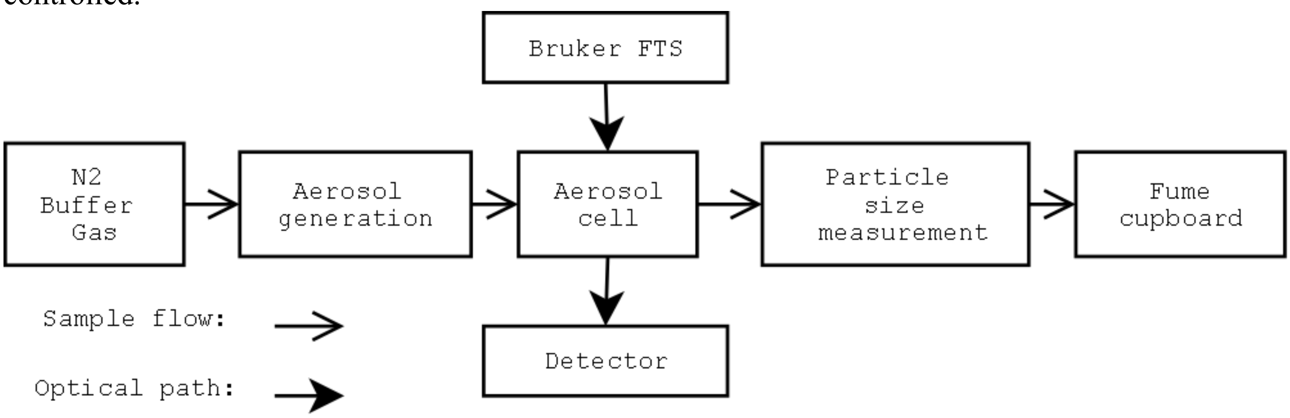

Figure 1. Simplified diagram of experimental configuration.

All of the measurements were undertaken at the Molecular spectroscopy facility at the Rutherford Appleton laboratory, a UK NERC funded facility. The aerosol cell used has an optical path length of 30 cm. Future work is planed to use a multi-pass cell to look at black carbon aerosol optical properties. Spectral intensity measurements are made using a Bruker FTS. Measurements of the detected spectrum are obtained with and without the aerosol to calculate the transmission spectrum, $T(\lambda)$. The method has been described in detail by Thomas (2005). A correction is made to the transmission spectrum to remove water and carbon-dioxide gas absorption lines; this was achieved via a separate retrieval of these gas species concentrations.

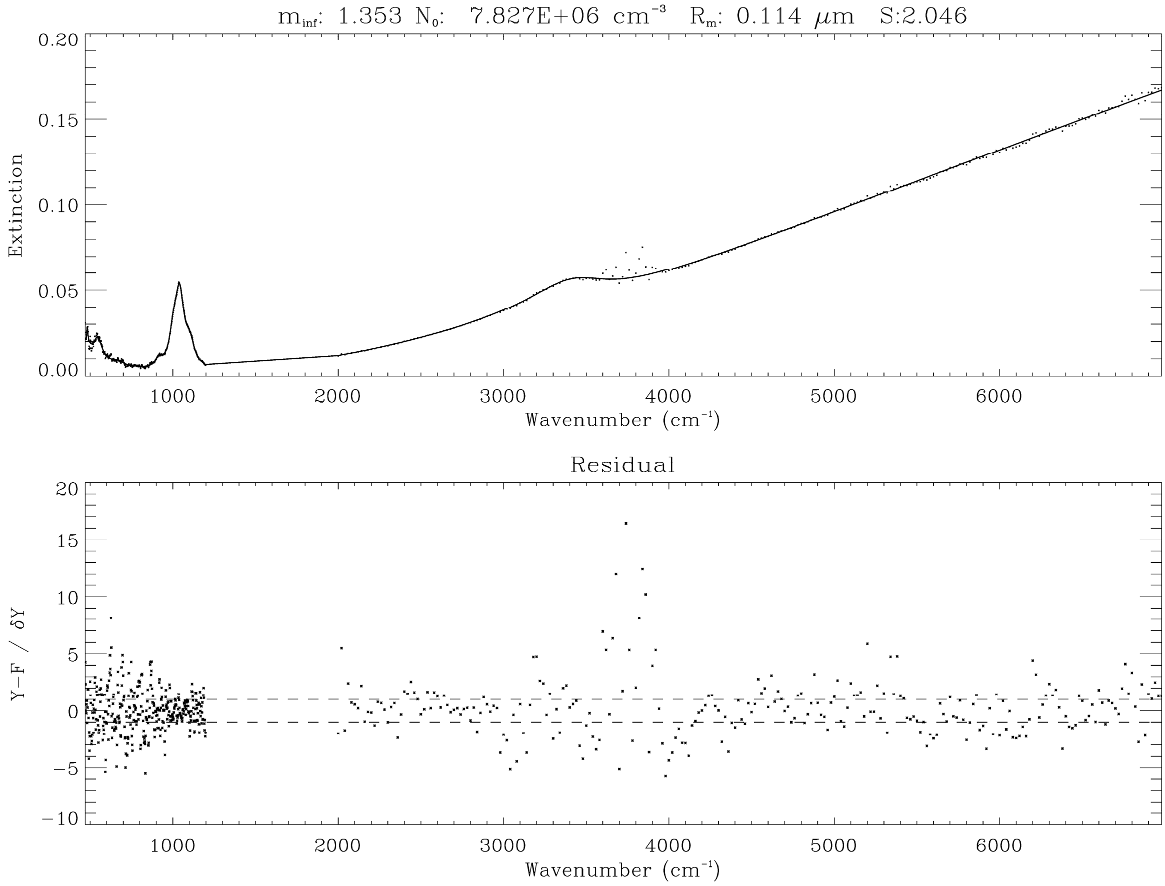

Figure 2. Top plot: Measured spectra (dots) and fitted spectra (lines). Bottom plot: fitted residual.

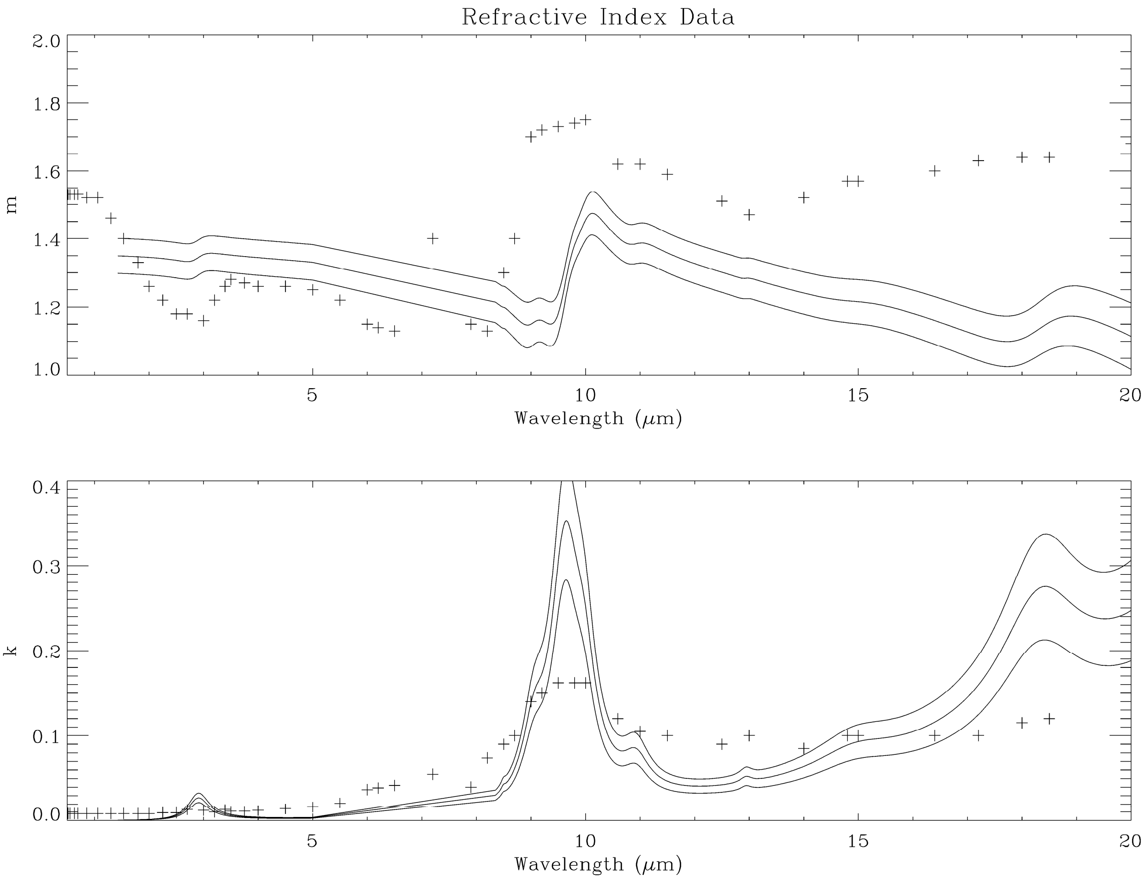

Figure 3. Inverted complex refractive example for Cape Verde dust (central black line). Surrounding two black lines indicates estimated uncertainties. Crosses show the existing published data [2]. Note these are still preliminary results.

2.2 *Results*

The refractive index of the aerosol from the measured absorption spectra has been determined using this method. This is the first time that the spectral dependent refractive index has been measured on a real mineral aerosol in the laboratory, past measurements are based on collected samples pressed into KBr pellets, for example Shettle (1979). An example of the measurement and forward model fit is shown in Figure , the associated refractive index in Figure . These are preliminary results; the final results may differ and will be published after further validation work. Further results have been published using this method by Irshad (2009) for sea salt aerosols.

3 A NOVEL INSTRUMENT

The angular scattering of radiation by a particle is not only dependent on its size and shape, but also on its refractive index. Traditionally, this dependence has been viewed as a hindrance to the performance of optical particle counters, as it requires assumptions to be made about the refractive index to allow size estimates to be calculated. Instruments such as the Wyoming OPC use white light and carefully positioned detectors to minimize the sensitivity of the instrument to particle refractive index (Dashler 2003). The SPARCLE instrument represents a shift in measurement principle to actively using this dependence to gain more information about the aerosol particles. Additionally, data analysis is performed on a particle-by-particle basis in the SPARCLE system. This enables the attribution of particles' sources (by their refractive index) to different size ranges this cannot be done using the Wyoming OPC system, where the returned data are simply the number of counts per channel.

3.1 *Method*

There are two key innovations that form the basis of the SPARCLE instrument. Firstly the use of a solid state detector array within a small, autonomous in situ instrument to provide a high resolution measurement of particle scattering on single particles. Secondly the analysis scheme employed by the instrument is completely original. This is to our knowledge the first numerical retrieval scheme which provides both the particle radius and the complex refractive index from a measurement of light in the Mie scattering regime. The development of such an algorithm and its application to actual measurements represents a new state-of-the-art in optical particle measurement.

Sensitivity to both refractive index and size allows measurement of the single scatter albedo on each particle (by assuming Mie theory). This is a significant advantage as SPARCLE is the first instrument to be able to make this measurement on single particles in the atmosphere.

3.2 *Results*

The instrument uses two detectors; a fast sensitive photomultiplier tube (PMT) and a linear detector array (LDA). The LDA records individual particle phase functions and the PMT measures over a wide angular range to provide sensitivity to the smallest particles. Thus the forward model; $\mathbf{F}(\mathbf{x})$ relates the detectors measured phase function via mie theory to the particle size and refractive index, the state vector $\mathbf{x}$. The optimal position of the detectors has been determined by calculation of the number of degrees of freedom to allow the highest instrument performance to be obtained i.e. the best ability to distinguish size and refractive index. The Figure demonstrates that real part of the refractive index and particle size are obtainable up to a lower size limit of around 0.1μm in radius. The real and imaginary parts of the refractive index and the particle size are available for particles sizes of 0.2μm in radius and above.

The current prototype instrument is able to detect and measure the phase function of test particles and has been field tested. Further work is required to increase the LDA sensitivity. The current set up is limited by digitization noise. Low noise pre-amplification is required to ensure the detectors are dark current limited hence obtaining the highest instrument sensitivity. The increased instrument sensitivity will allow the instrument to reach it's full potential in determining single particle optical properties.

4 CONCLUSIONS

Two examples of the application of optimal estimation our given. The Aerosol refractive index of Cape Verde dust has been successfully retrieved. The method is unique as it provides spectrally resolved refractive index data from a real aerosol, current published measurements have only been made on bulk samples. This work is soon to be expanded to include black-carbon aerosol. This will allow the investigation of the applicability of the widely used of mie theory, which assumes spherical particles to predict the radiative forcing of this aerosol type despite it being fare form spherical. A novel method to determine individual particle refractive index has been describe, and this is very much work in progress (subject to funding). The method shows potential to determine single scatter albedo, particle refractive index and size on individual particles for the first time. These new methods show great potential in characterisation of transport particulate (in particular black carbon) emissions from transport sources both in the field and for laboratory studies.

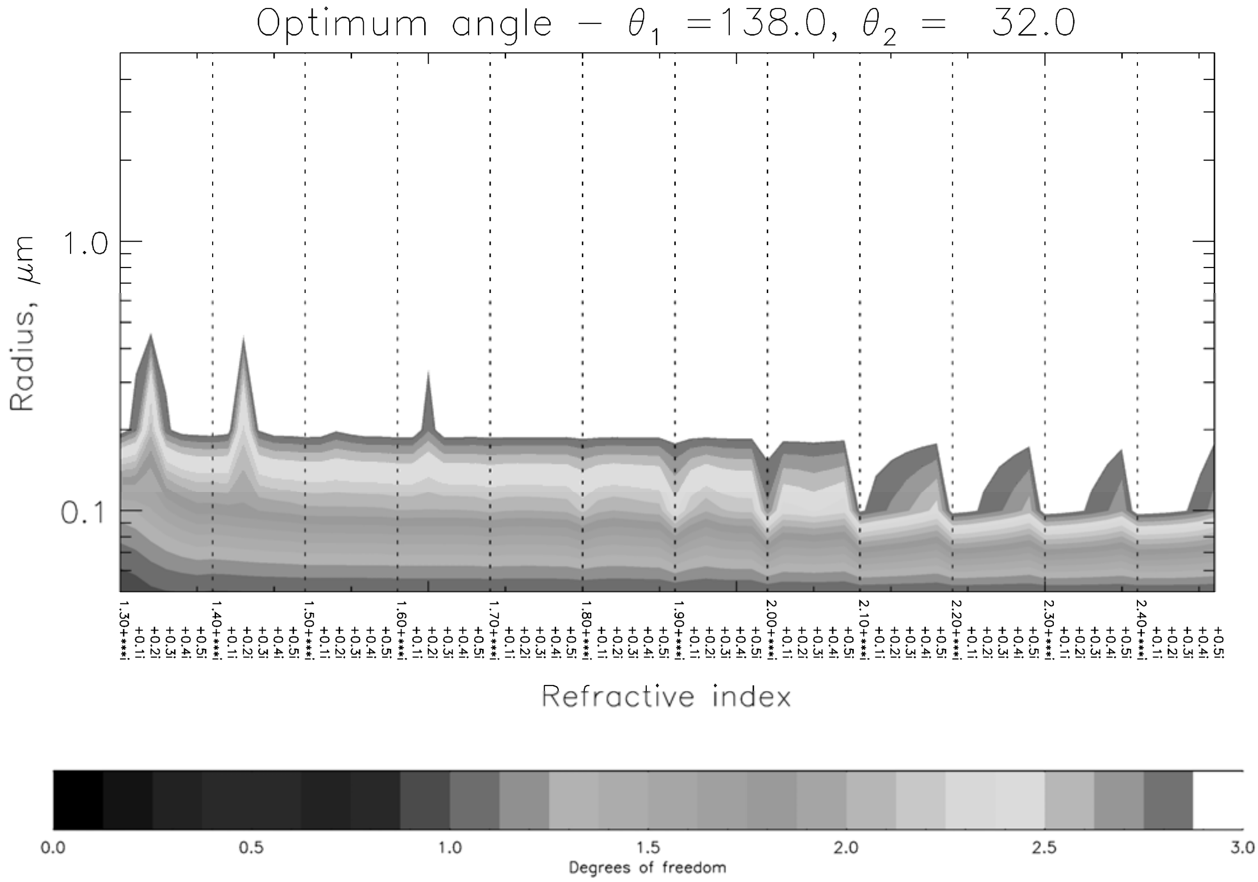

Figure 4. Optimal instrument calculated performance.

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