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Single Particle Raman Spectrometer



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This project seeks to develop a prototype system for the analysis of single levitated micrometre-sized particles captured from an ambient aerosol. The system is designed to use Raman scattering to establish chemical nature of the particle, whilst simultaneously recording spatial elastic light scattering data from which an assessment of particle size, shape, and physical structure may be achieved. This multi-parametric approach should provide a means of discriminating atmospheric particles whose toxicity is determined by morphology as well as chemical composition. Areas of application could include environmental monitoring, source apportionment, occupational air-quality investigation, and potentially as part of a strategy for bio-aerosol detection.

The prototype SPaRS comprises several distinct sub-systems: a particle charging of particles down to micrometre-sizes for their entrainment and capture from a sample aerosol flow; an electrodynamic levitation chamber capable of holding the captured particle essentially stationary whilst measurements are recorded; a diode laser particle illumination system; a Raman scattering spectrometer; and a spatial light scattering acquisition sub-system. Integration of the sub-systems to complete a laboratory prototype is underway and the use of the system will continue under a DSTL funded studentship (Dalley).

Particle Charging and Trapping

Single particles drawn from the ambient air are held still in an electrodynamic balance (EDB) for analysis. To capture and hold them adequately, particles must be charged sufficiently to enable them to be trapped in the EDB's electric field. The AC unipolar charger used in this instrument provides a very effective method of charging particles. Initially, the charged particles will be collected on a grounded plate, and then selected with a tungsten needle and launched through a hole in the top of the trap. Further work, possibly using electrostatic focusing should lead to more automated sampling.

Charger Description

The AC unipolar charger[1], shown schematically here (fig 1), uses two arrays of sharp needles pointing towards each other across the aerosol flow which is directed along the middle of the charger between two grids. By applying a voltage gradient between one set of needles and the grids (electric field ~3kV/cm) in the first half cycle of the applied AC square wave, the ionised air molecules from one needle tip are attracted across the aerosol flow; in the second half cycle the process reverses. Aerosols passing through the charger are highly charged as the particles are bombarded by many cycles of ion flux. When charged, the particles drift across the charger due to the electric field, and as the applied field reverses so does the drift direction and the particles trace out a zig-zag or W shaped path as shown in fig 2.

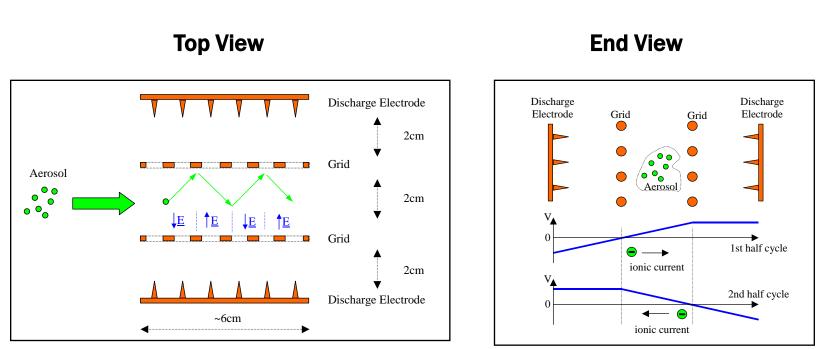
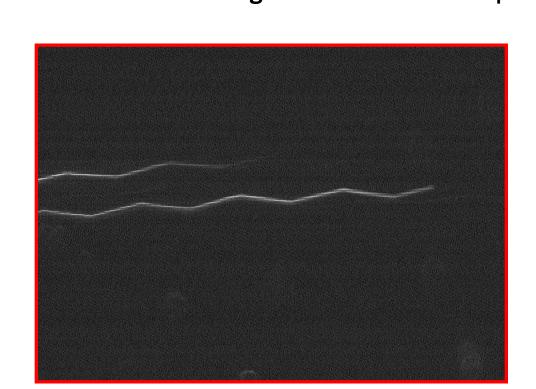
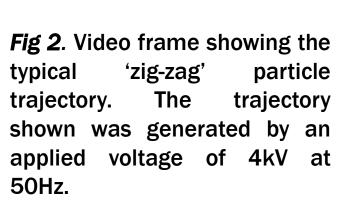


Fig 1.Schematic of AC unipolar charger.





DC cup electrodes **AC** electrodes Fig 3. Cutaway of Electrodynamic Balance (EDB).

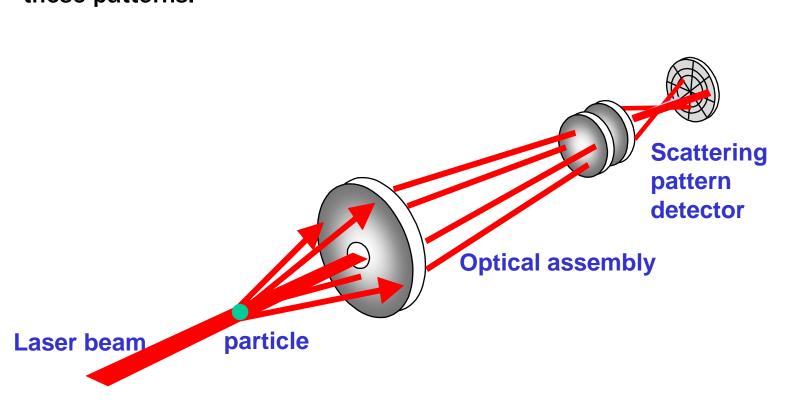
Particle Trapping

An individual particle is launched from an overhead needle into the particle trap. The conical AC electrodes of the trap form an electrodynamic balance (EDB) keeping the particle central [2] . The outer DC cup electrodes enable the particle to be moved up to counter the effect of gravity. Viewing windows at the top and bottom allow forward and backscattered light to be acquired.

Spatial Scattering

The spatial distribution of light scattered by a particle, often called the scattering profile, is a complex function of the size, shape, structure and orientation of the particle, as well as of the properties of the illuminating radiation (wavelength, polarization state).

The authors have developed a number of techniques based on the acquisition and analysis of the forward scattering profile of single micro-particles. The basic configuration is illustrated schematically below (fig 4); example scattering patterns are also shown (fig 5). Previous research at UH [3] has demonstrated that individual airborne particles can be characterized or classified by analysis of these patterns.



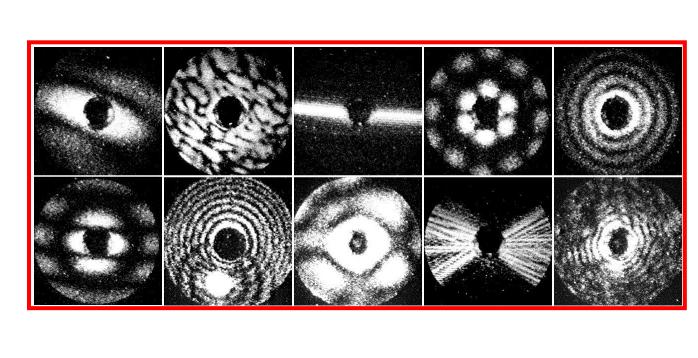
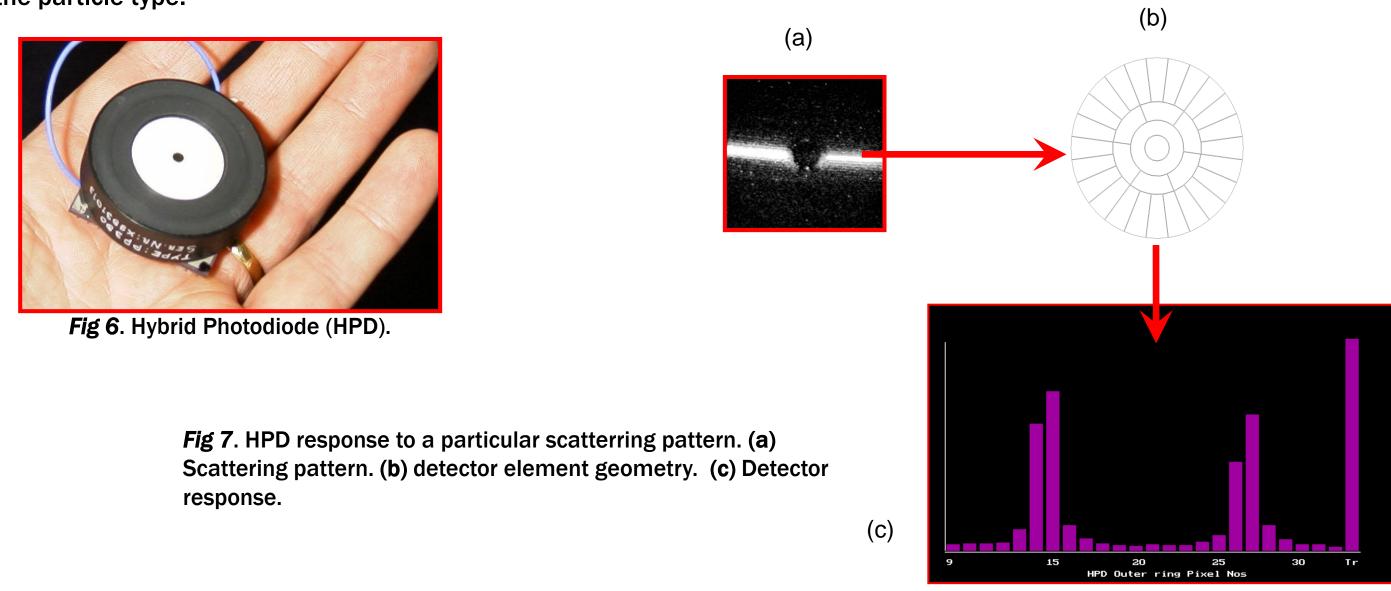


Fig 4. Spatial scattering optical configuration.

Fig 5. Example scattering patterns.

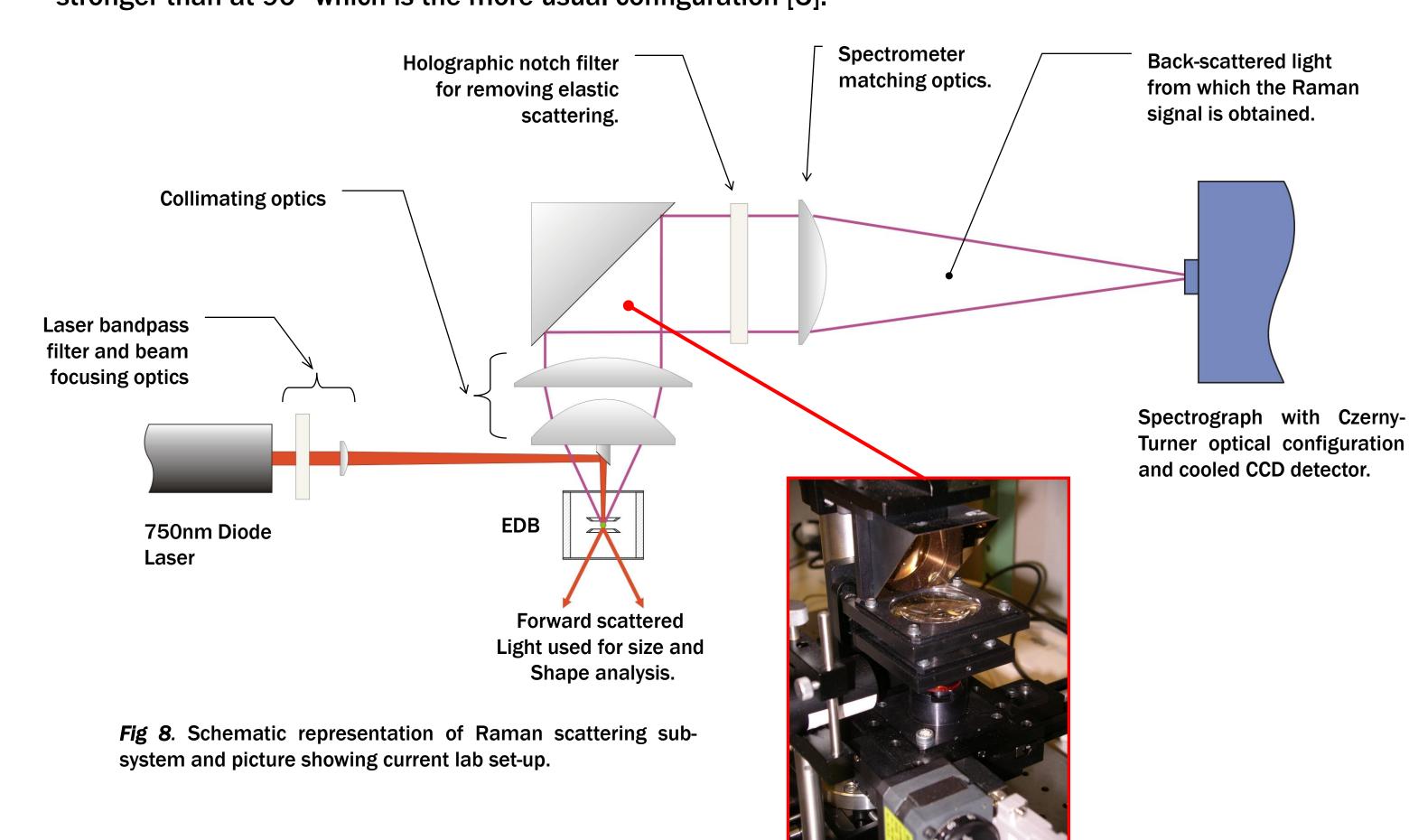
Whilst the example scattering patterns shown in fig 5 were recorded using an intensified charge-coupled device camera, SPaRS will use a far cheaper and more compact imaging device called a hybrid photodiode or HPD (fig 6). The custom HPD for use in SPaRS records scattering patterns using a radial array of pixels. The geometry of this array is shown in fig 7 (b) which illustrates the response obtained from a particular scattering profile. The output from the detector (fig 7 (c)) will be analysed (possibly employing artificial neural network pattern matching) to provide data on the shape and size of the particle in the trap with a view to classifying the particle type.



Raman Scattering Acquisition

The Raman effect is an inherently weak phenomenon with scattering cross-sections typically several orders of magnitude lower than other phenomena such as fluorescence which can entirely swamp the signal. The Raman spectrometer system developed here uses a number of technologies and design features to maximize the signal and fulfil the other requirements of the project.

- 1. The use of a Near Infra-Red (NIR) laser diode emitting light at 785nm significantly reduces fluorescence background [4].
- 2. A holographic notch filter (HNF) is employed to remove the Rayleigh scattering from the signal prior to the spectrograph. An HNF has a high transmission of all wavelengths outside the 'notch' and a very high optical density inside the notch. Its other chief characteristic is that the filter edges are very sharp so in principle it is possible to look at Raman signals close to the wavelength of the laser.
- 3. A CCD detector with thermoelectric cooling down to -60° (or greater if necessary) allows long exposure times without the detector saturation problems.
- 4. A back scattering configuration is used which, as well as facilitating simultaneous Raman and Rayleigh scattering acquisition, improves the signal-to-noise performance because the back-scatter Raman signal is stronger than at 90° which is the more usual configuration [5].



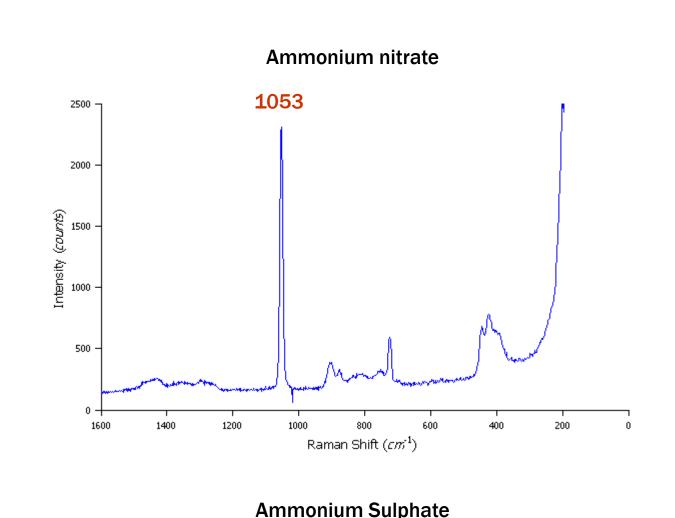
Preliminary Results

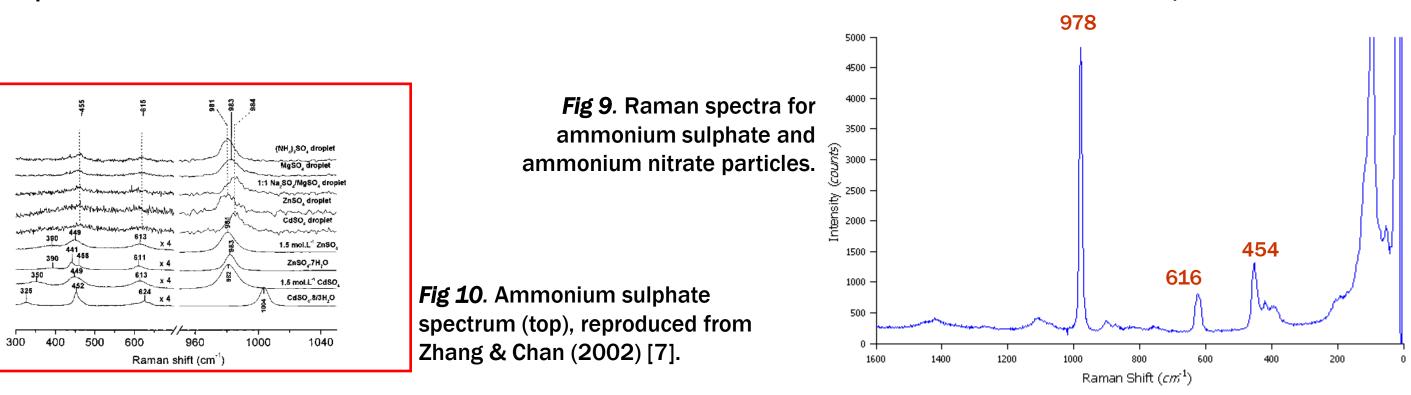
Although the EDB is not yet integrated into the system, the Raman spectrometer has been tested with single particles of ammonium nitrate and ammonium sulphate loaded onto a tungsten needle. Both spectra were obtained from 30s exposures.

The ammonium nitrate shows a strong line at 1053 cm⁻¹ corresponding to the NO₃⁻ stretching mode reported by Musick et al

The three lines identified in the ammonium sulphate spectrum correspond to those reported by Zhang and Chan [7], reproduced below (fig 10).

The large signals present near the laser-line are mostly due to the background generated by the tungsten needle. Experiments with sulphur grains clearly reveal the 85 cm⁻¹ line showing that sub-100 cm⁻¹ spectral lines are resolvable.





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Summary System for multi-parametric analysis of ambient aerosols. AC unipolar charger and Electrodynamic balance subsystem for capturing sampling and trapping particles.

 Sub-system for capturing forward scattering for shape and size analysis.

 Raman spectrometer sub-system for chemical analysis generating first results, indicating good sensitivity and fluorescence suppression.

 Integration of various components underway. Further development and use of the instrument will continue under a DSTL funded studentship (Dalley).

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