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Opportunities for Raman and Near-Infrared Spectroscopy in On-line Characterisation

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Clever Characterisation for Smarter Formulation , RSC, 10th November 2017

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Motivations/Challenges

1. How to transfer standard off-line techniques to on-line/ in situ?

   Low sensitivity techniques such as near-IR or Raman spectroscopy for measurements in formulation

   Off-line measurements – interrupts process, sample can change, requires skilled operators, often expensive

   Shorten development times

   Improved reproducibility in manufacturing – quality control

2. How to obtain: Composition – bulk and trace components
   Physical properties (Proxy-measurements) eg. particle size distributions

3. How to get representative samples?

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Plan

1. Introduction and Motivations
2. On-line optical diagnostics in formulation
3. Near-infrared spectroscopy
4. Raman spectroscopy
5. Light-induced fluorescence spectroscopy
6. New projects and future directions
7. Summary and conclusions

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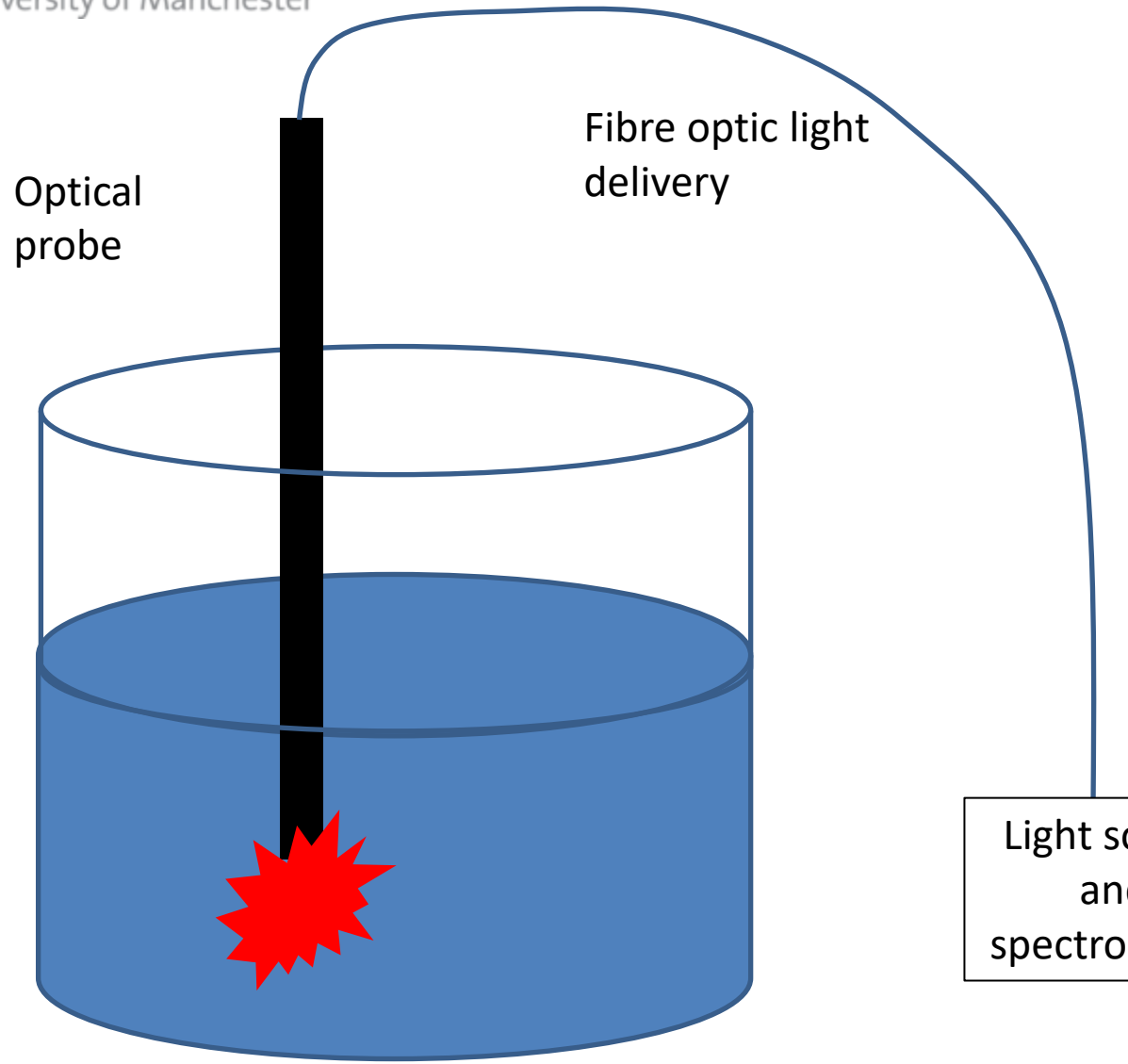
2. On-line and in situ optical diagnostics

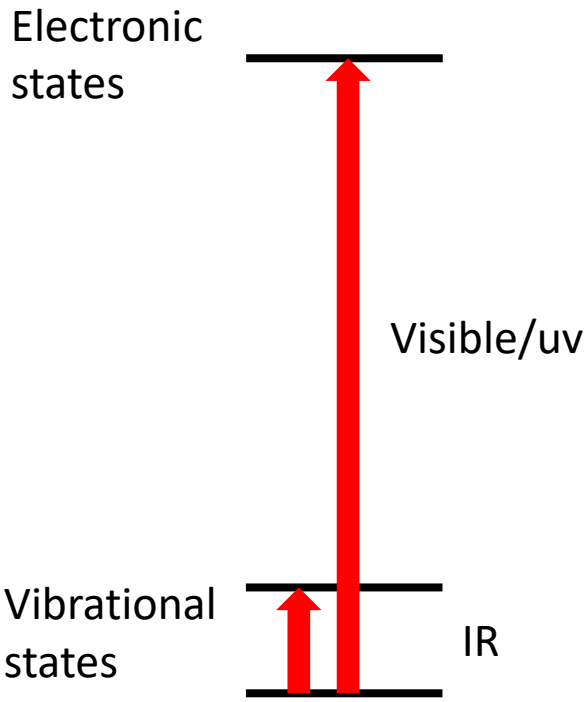


Light scattering

Light absorption

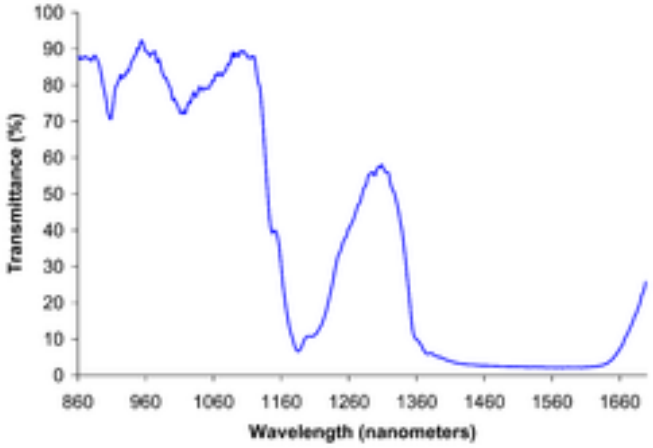
UV, visible, IR

What is near-infrared (NIR) spectroscopy?



- Absorption spectroscopy (4000 – 12000 cm^{-1})
- Weak transitions based on overtone and combination vibrational bands
  - O – H
  - C – H
  - N – H
- Minimal distinct features
- Requires multivariate analysis
- Robust process analysers

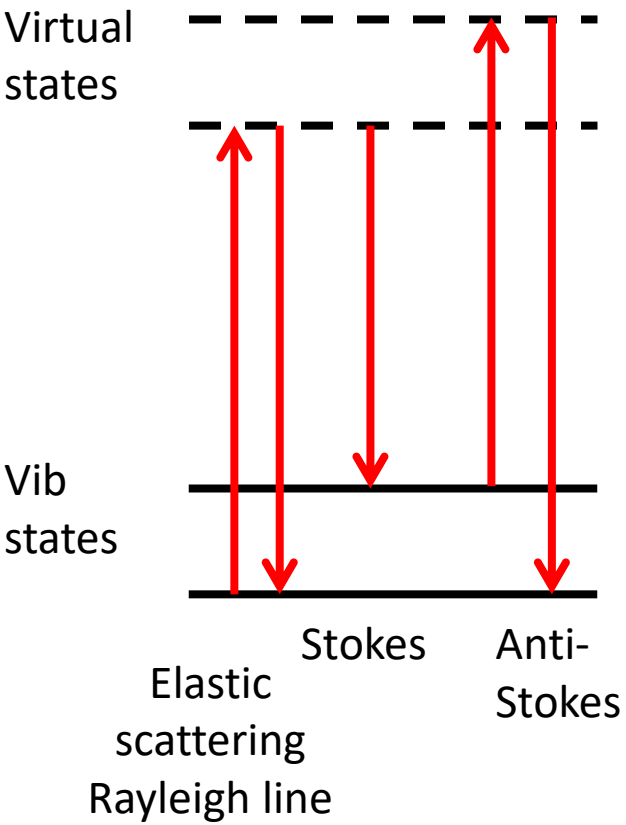
Beer-Lambert law

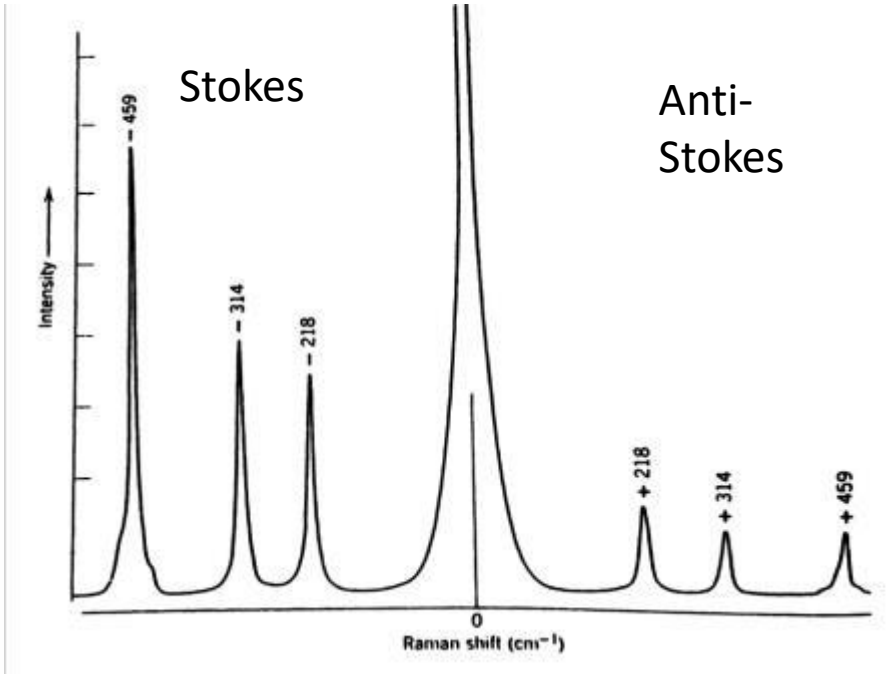


Near-IR spectrum of ethanol

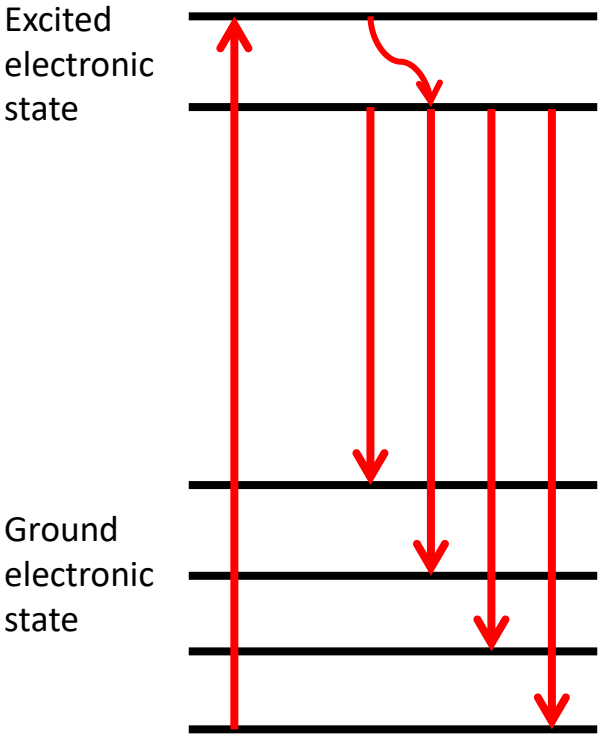
What is Raman Spectroscopy for Process Analysis?

- Inelastic scattering
- Weak effect
- Wavelength dependence $1/\lambda^4$
- Due to change in polarisability of molecule
- Vibrational transitions (usually different to IR)
- Accompanying fluorescence problematical

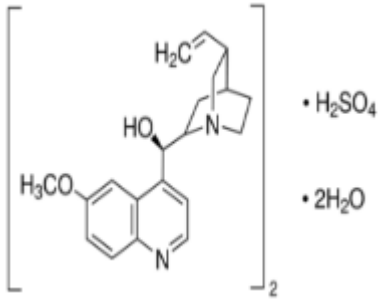


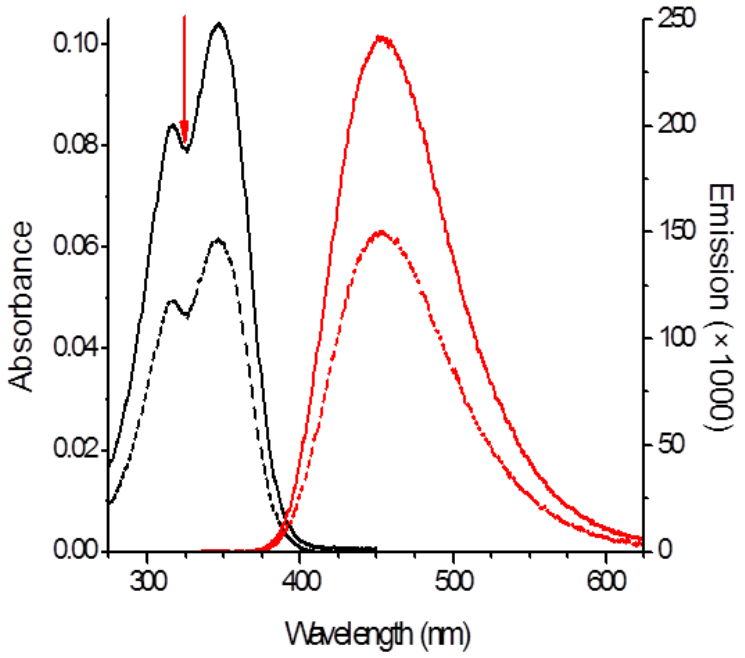


What is fluorescence analysis in process analysis?



Example: quinine sulfate in 0.05M H_2SO_4





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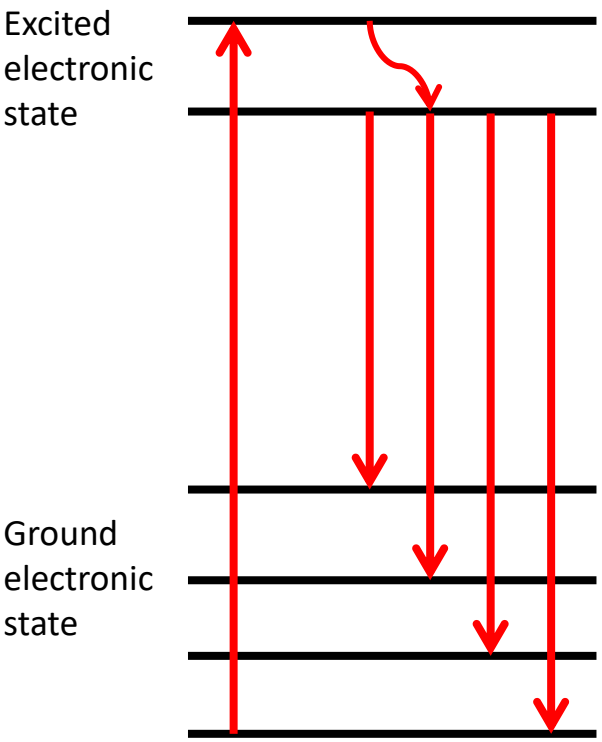
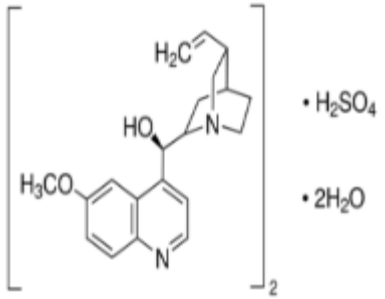
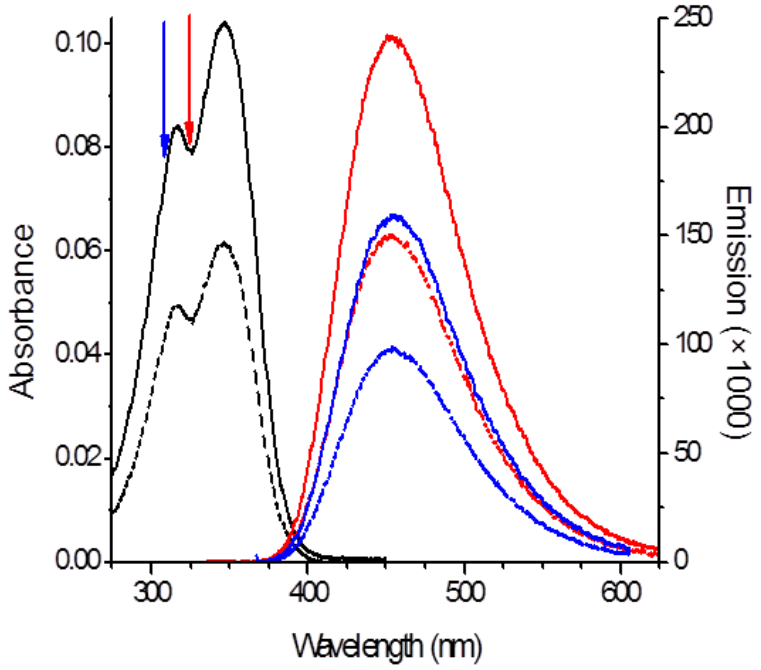


Excitation at λ

Fluorescence to lower electronic state





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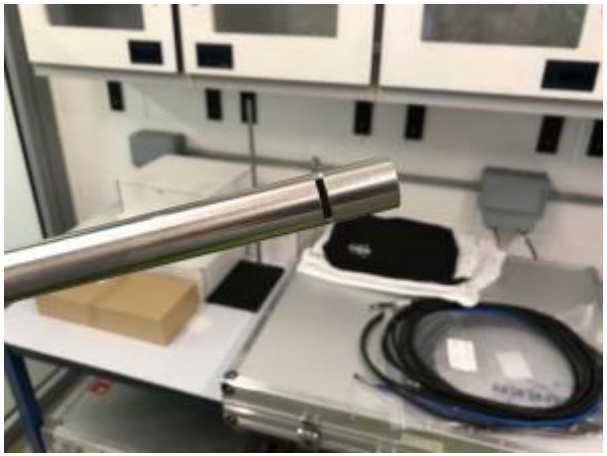
Near-IR Process Analysis

- All samples measured using a Bruker Matrix F FT-NIR spectrometer with an immersion transmission probe with a 2mm path length.
- Samples were measured at a resolution of $4cm^{-1}$ and three repeats of each sample taken.



Difficulty of getting homogeneous sample into gap

Too wide and light is totally absorbed. Too narrow and light absorbance is too small

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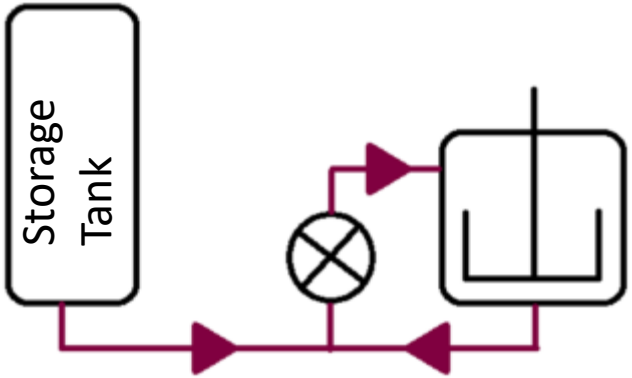
Placing the in-line measurement probe

- SLES enters the process through a high shear device in the recycle loop.
- For greatest representation of dilution the probe was placed in the mixer rather than in the recycle loop



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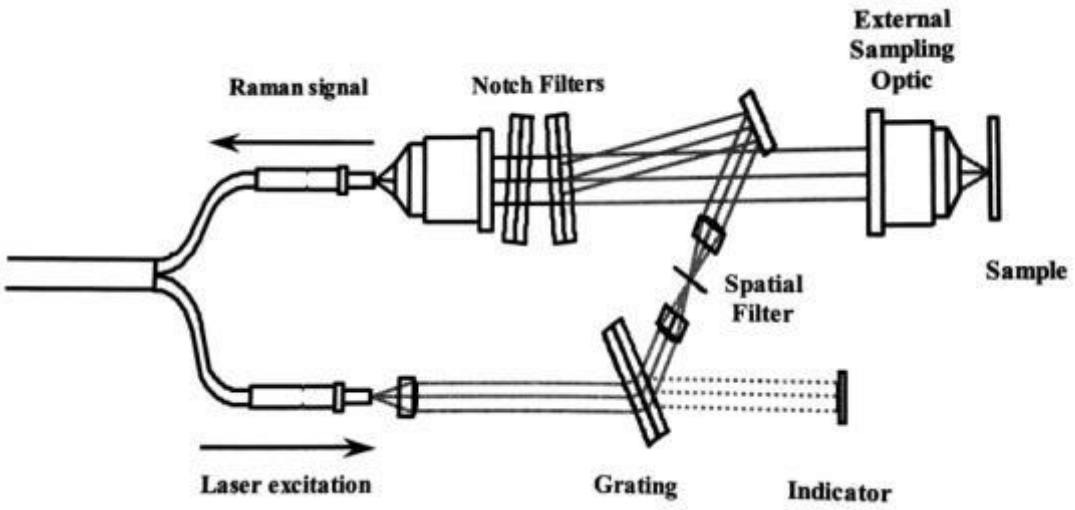
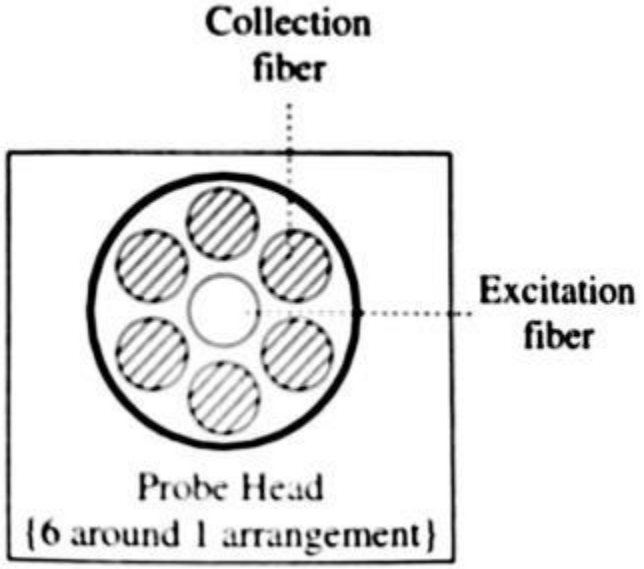
4. Can Raman spectroscopy be used for SLES measurements?

Simpler probes than for absorption

- Immersion probes
- Phat probe
- Non-contact probe
- Microscope objective

Kaiser Optical System RXN1 Spectrometer
785 nm excitation (400 mW)





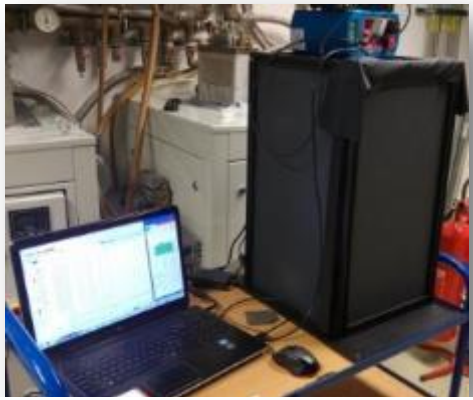
Development of On-Line Raman Spectroscopy in the Aerospace Industry

On-line Raman probe measurement

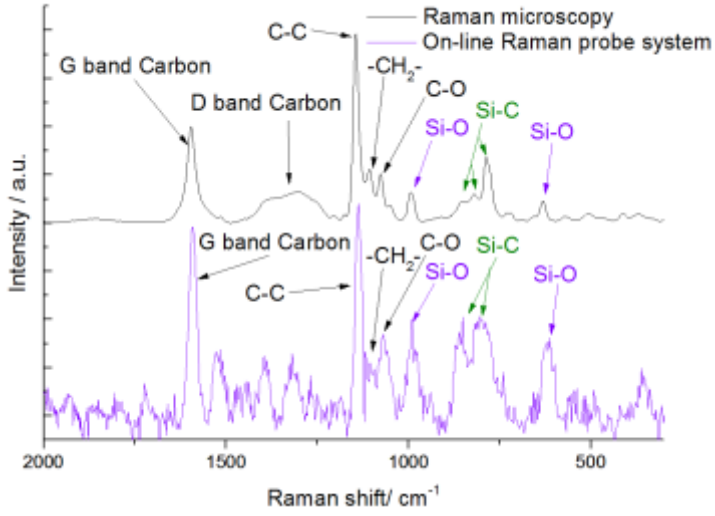
785nm spectrum stabilised laser
Max output = 499mW

Raman excitation and
collection probe.
Operating distance = 7.5mm

QE pro Raman spectrometer
Range = 0cm^{-1} – 2850cm^{-1}
Res. = ~3cm^{-1}



- The probe system developed here (UoM) has a lower resolution as well as suffering from less intense scattering.
- Due to lower signal to noise ratio, we can't use univariate so must use multivariate.
- Transfer from off-line Raman microscope to on-line probe.



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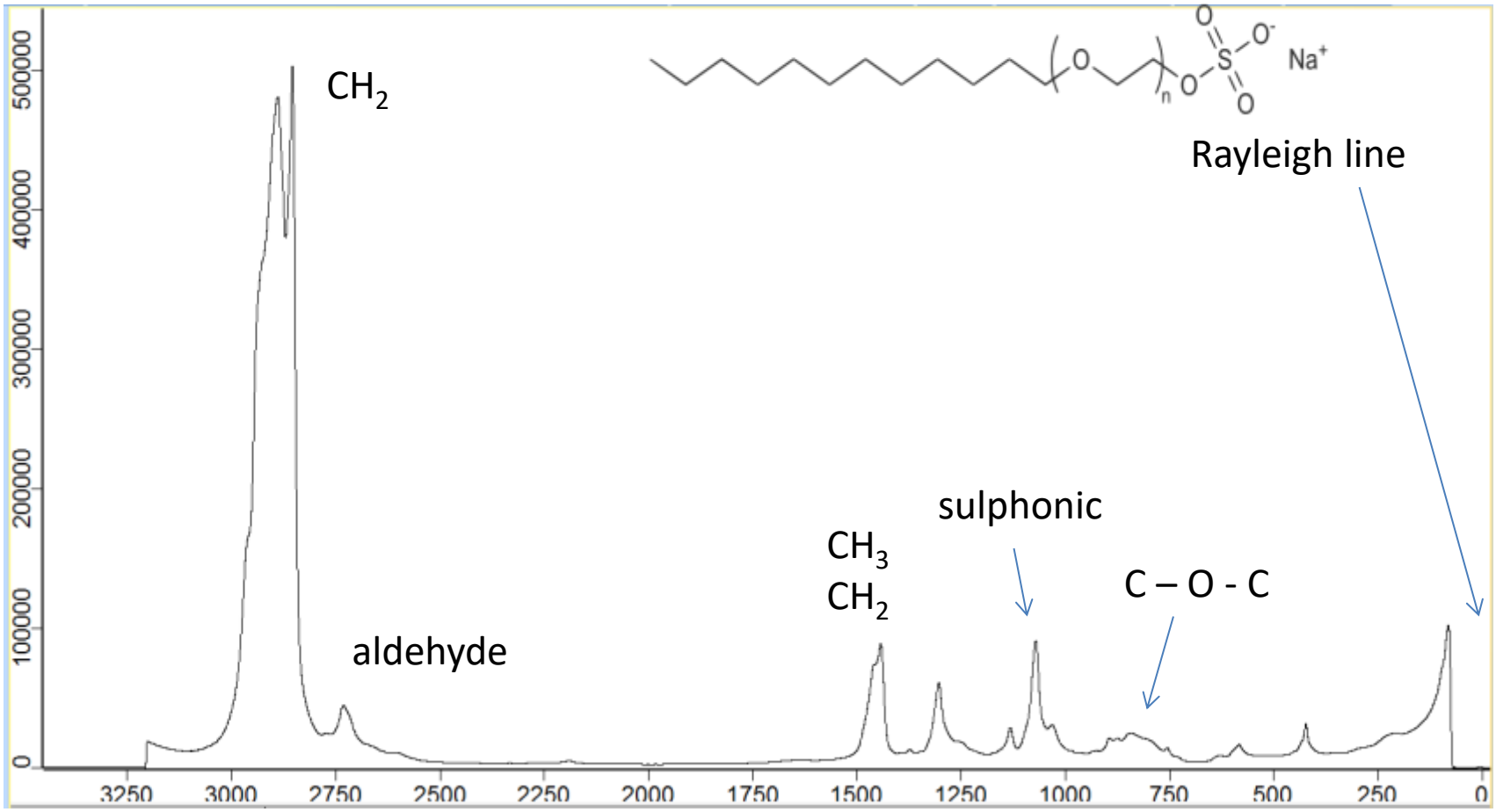
Raman spectrum of SLES (785 nm excitation)



Small variations in spectra with probe position

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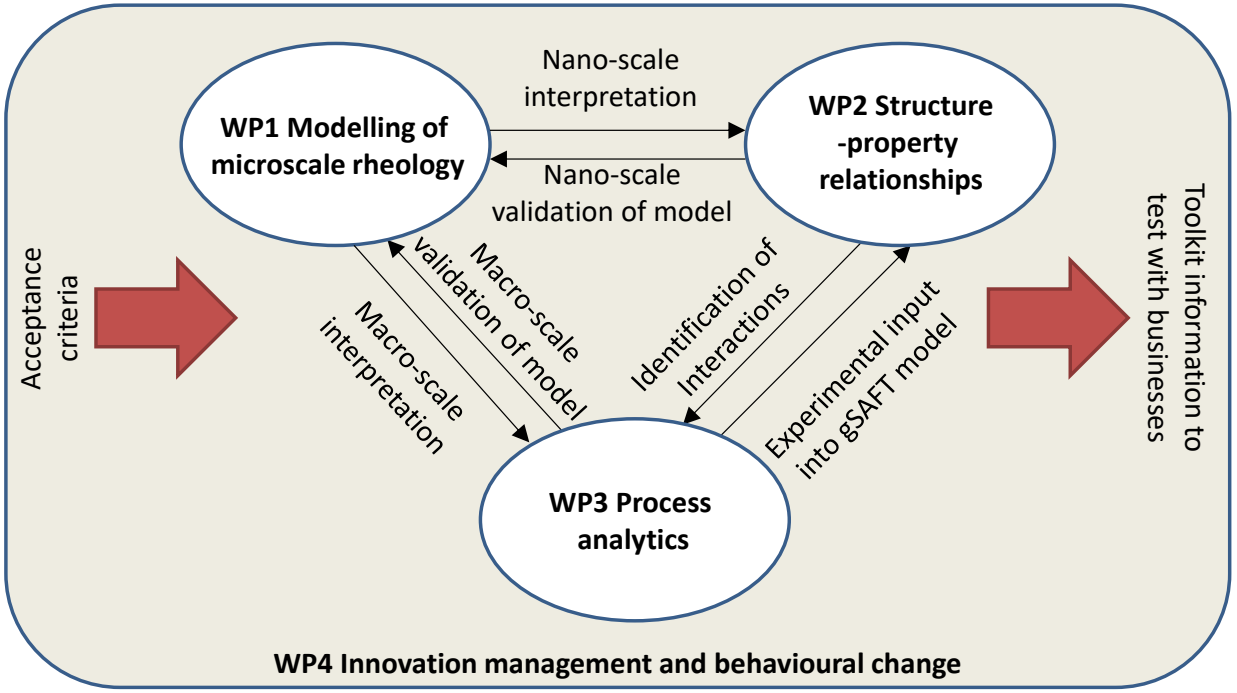
6. Centre in Advanced Fluid Engineering for Digital Manufacturing (CAFE4DM)



£6.5M 5-year project

Prosperity Partnership

Unilever

EPSRC
Engineering and Physical Sciences Research Council

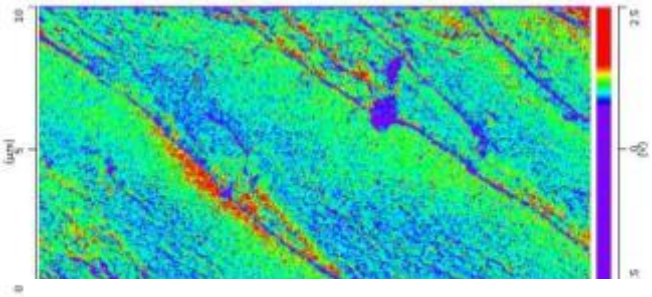
This 5 year project aims to address the challenges in understanding, creating and scaling up manufacturing processes for formulated products

PDRA Positions available

PhD studentships available

6. New Raman projects

3D Confocal Raman Microscopy in membranes for fuel cells and molten salts



Preliminary Nano-IR results of a freeze fractured Nafion 117 membrane. Ratio of CF_2/SO_3 bands

In direct methanol fuel cells methanol crossover is a key inhibitor to their success

Preliminary results have shown the feasibility of using confocal Raman microscopy to measure methanol in a free standing Nafion membrane in 3D for determining the real-time chemical distributions.

Time-dependent studies will be made by pulsing CH_3OD samples.

Depth limitation of this will be of the order 120-170 microns and it is proposed to complement this with the new technique of Spatially Offset Raman Spectroscopy (SORS)

Manchester
UCL
Newcastle

EPSRC
Engineering and Physical Sciences Research Council

£1.6M

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6. Summary

- Shown that near-infrared absorption, Raman scattering and light induced fluorescence can be used for on-line measurements of composition and other properties in formulated products
- Sample probes of key importance – fibre optic beam delivery
- Must combine with multivariate analysis (correlation)

1. Development of infrared laser process analysers e.g. with spin-off company, TDL Sensors Ltd (www.tdlsensors.co.uk)

TDL Sensors Ltd

2. Centre for Process Analysis and Control Technology (www.cpact.com)

CPACT

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