Uranium Measurements by Time Resolved Laser Induced Fluorescence Spectroscopy

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Outline

- Background
- Project objectives
- Fluorescence of uranium
- What is fluorescence and why is it useful?
- Instrumentation at Loughborough
  - Limit of detection
  - Types of sample
- Future work
- Summary

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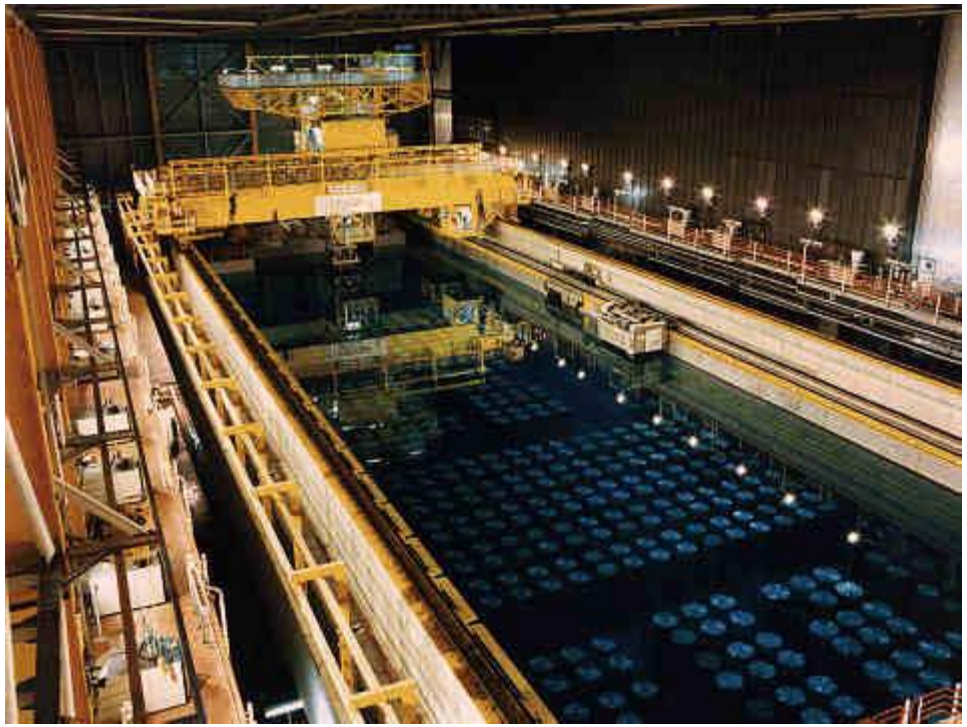
Background

- UK has a significant amount of spent fuel
- Wet storage
- Need for a mechanistic understanding of fuel dissolution processes
- Speciation



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Project objectives

- Setup a state of the art TRLFS system at Loughborough optimised for Uranium
- Determine speciation of uranium species
  - Library of reference spectra
- To develop spectroscopic methods for improved determination of SNF dissolution and corrosion rates in water

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Fluorescence of uranium

- Has been known for a long time
- Used in Paints and glass

What is fluorescence and why is it useful?

Fluorescence

noun

the visible or invisible radiation produced from certain substances as a result of incident radiation of a shorter wavelength such as X-rays or ultraviolet light.

the property of absorbing light of short wavelength and emitting light of longer wavelength.

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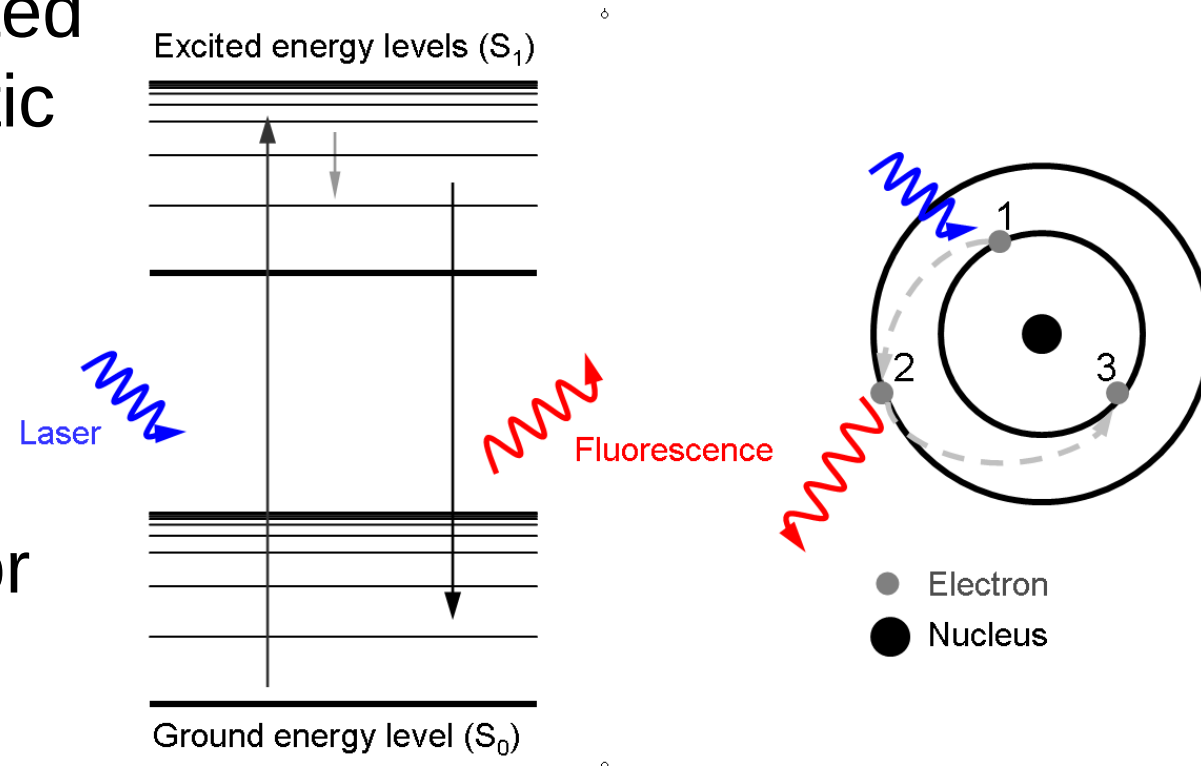
What is Fluorescence and why is it useful?

- Matter absorbs light.
- Electrons promoted to higher energetic states.
- On relaxation, compounds can emit light (luminescence) or decay non-radiatively.



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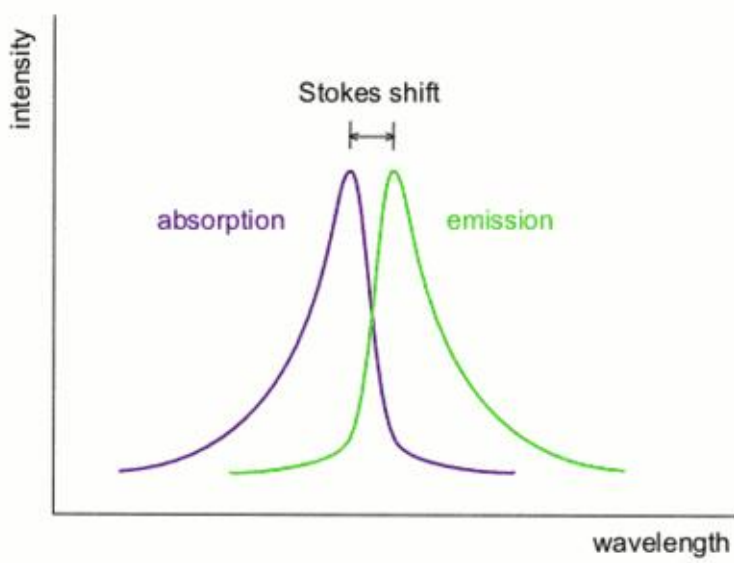
What is Fluorescence and why is it useful?

- Characteristic excitation and emission spectra
- Stoke shift (low background)
- Sensitive to changes in co-ordination environment
- Emission spectra and lifetime data are orthogonal to each other allowing for fingerprinting



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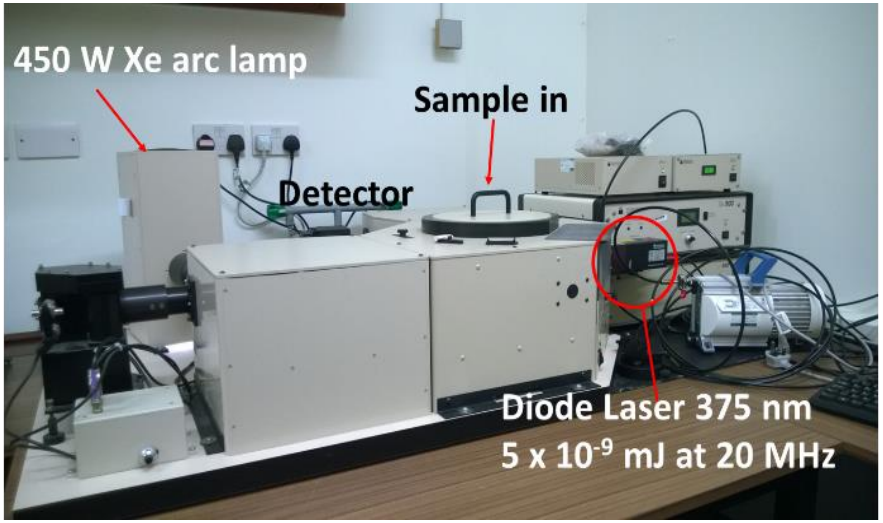
Instrumentation at Loughborough

- Edinburgh instruments FLS900
- Off the shelf instrument
- 375 nm diode laser / Xe arc lamp as excitation source
- Time correlated single photon counting (TCSPC)



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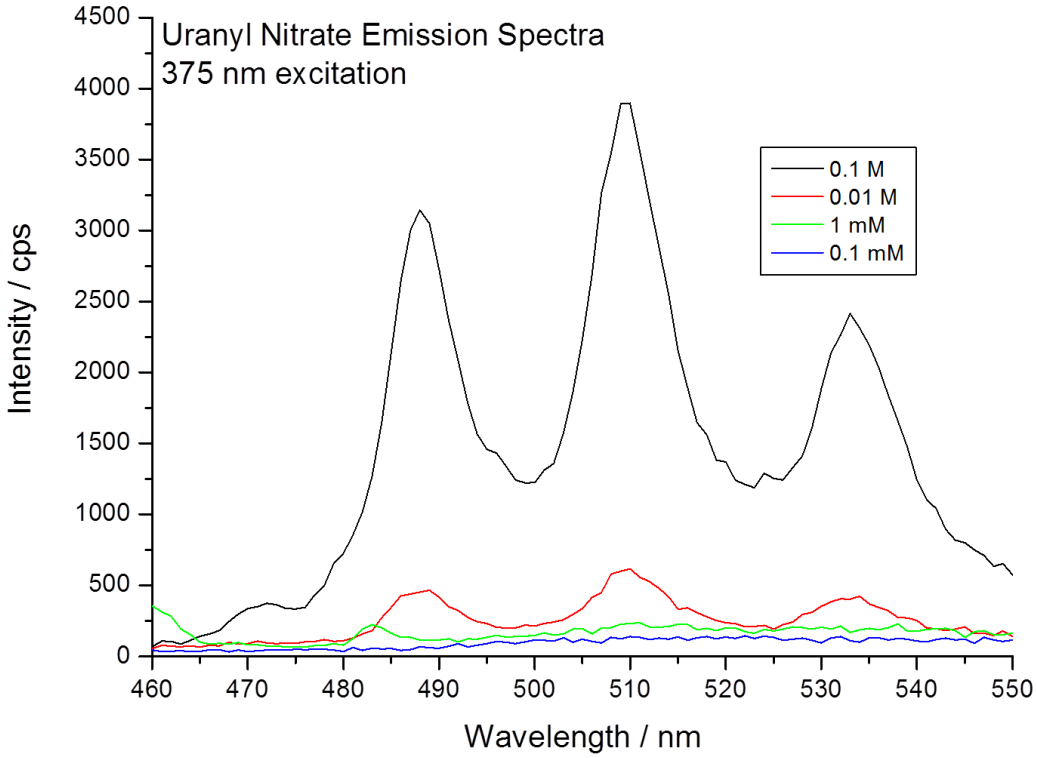
Initial uranyl nitrate measurements

- Samples were prepared in a nitrogen glove box
- pH was fixed at 2
- Range of concentration form 0.1- 1 x10^{-4} mol L^{-1}
- Samples placed into 4 cm $^{-3}$ plastic cuvettes
- Fitted with a stopper and sealed

Initial uranyl nitrate measurements

- Characteristic uranyl emission spectra obtained
- Agrees with literature
- Nitrate ion appears to quench fluorescence and increase the background



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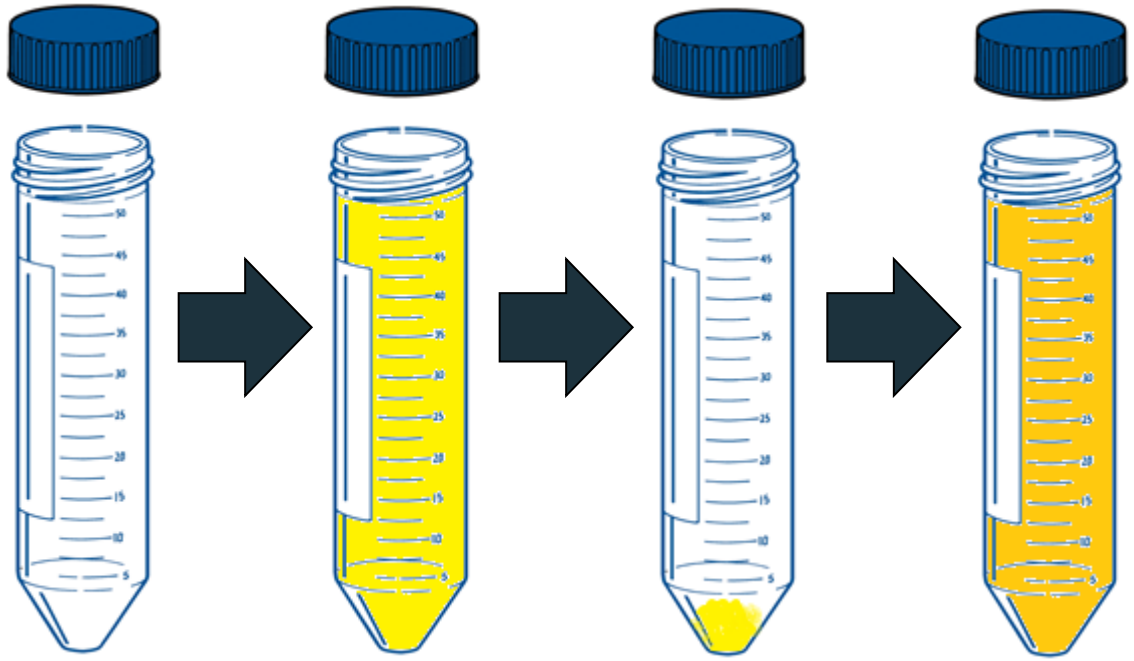
Nitrate removal

- Aqueous uranyl nitrate solution
- 0.5 mol L-1 NaOH added
- $Na_2U_2O_7$ precipitated
- Dissolved in perchloric acid



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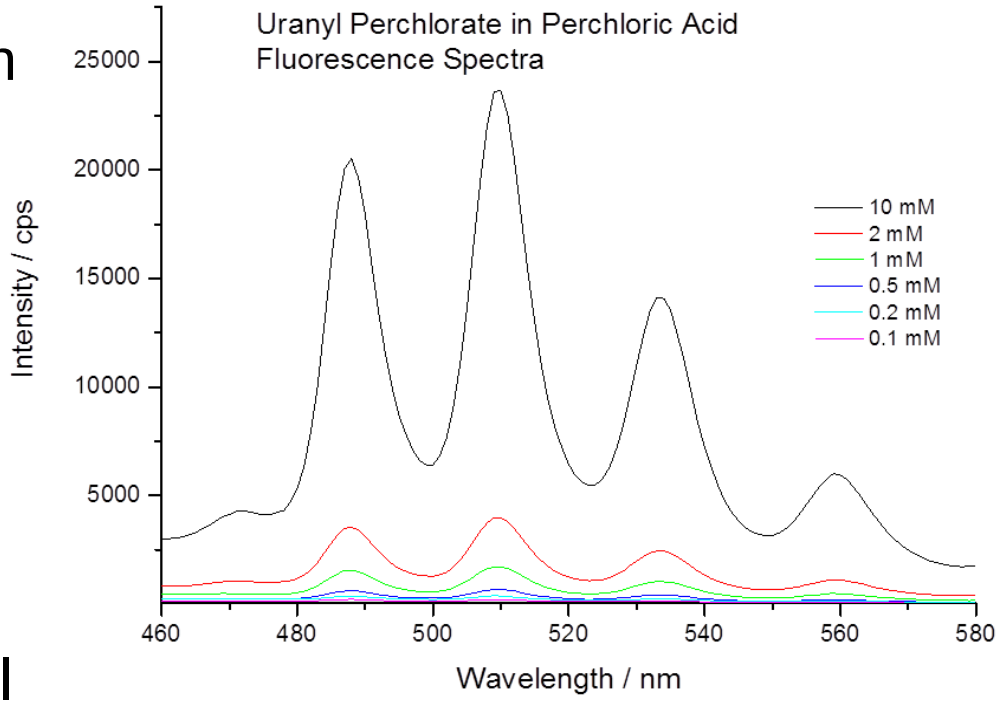
Limit of detection

- Limit of detection from literature $1x10^{-12}$ mol L^{-1}
- Current limit of detection $1x10^{-6}$mol L^{-1}
- Beginning to loose structure in spectrum
- Further optimisation required
- Increasing signal may loose resolution
- Energy of laser potential limiting factor for sensitivity



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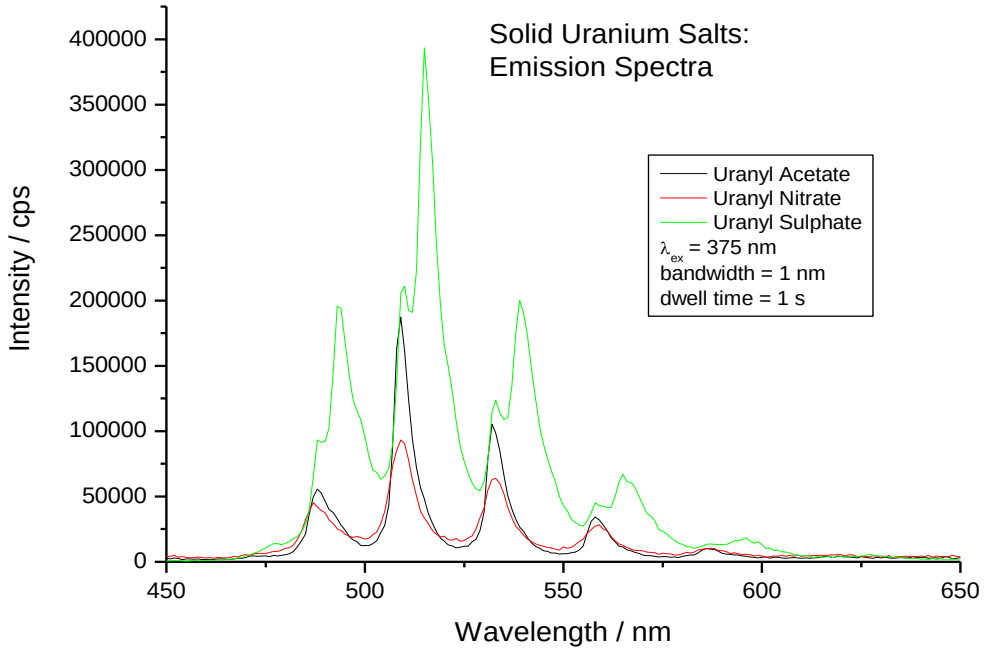
Solid uranyl compounds

- Nitrate, Acetate and sulphate all clearly visible with noticeable differences in their spectra.



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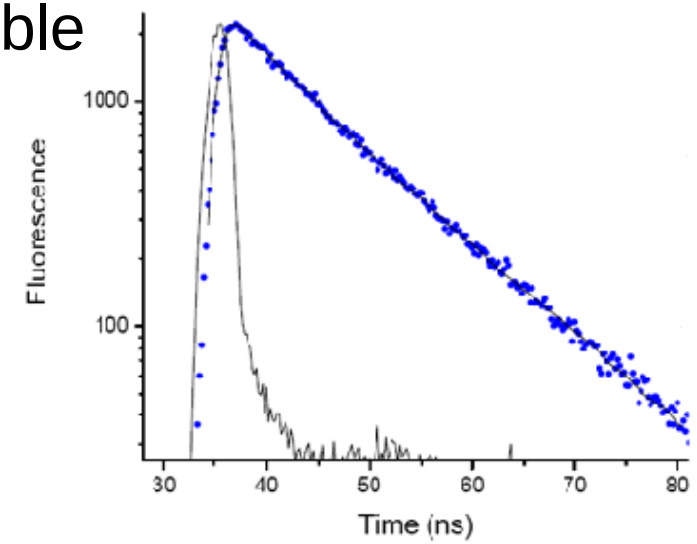
Fluorescence lifetime

- Time resolved data
- Rate of decay is inversely proportional to fluorescence lifetime
- Fluorescence intensity measured as a function of time 0 – 10 us
- See if time resolved data is possible
- Important for spectral mapping
- Compare with literature data



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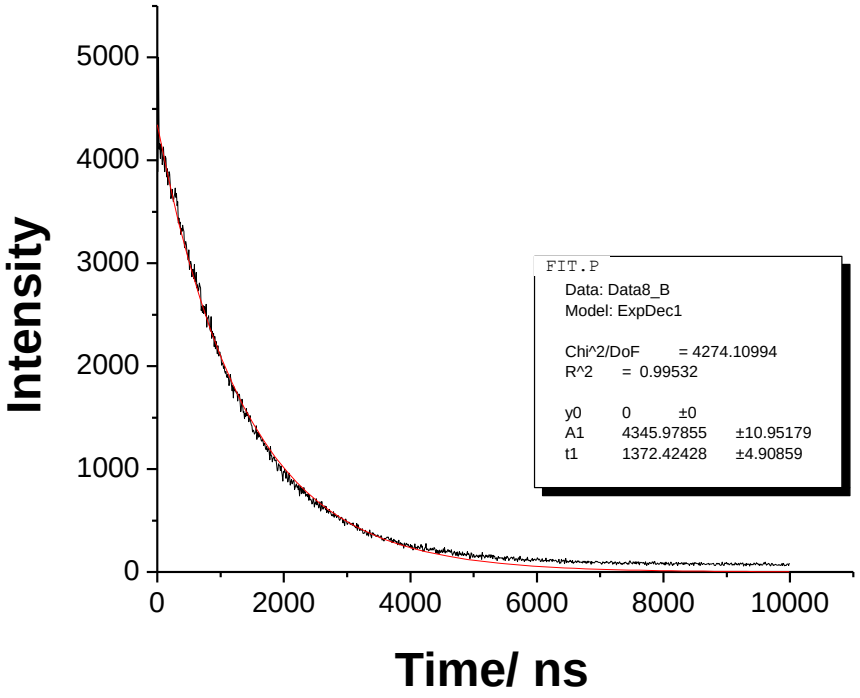
Fluorescence lifetime

- Smooth decay curve observed
- Single exponential fitting
- Relatively long lifetime
- 1.372 µs
- Comparable to literature



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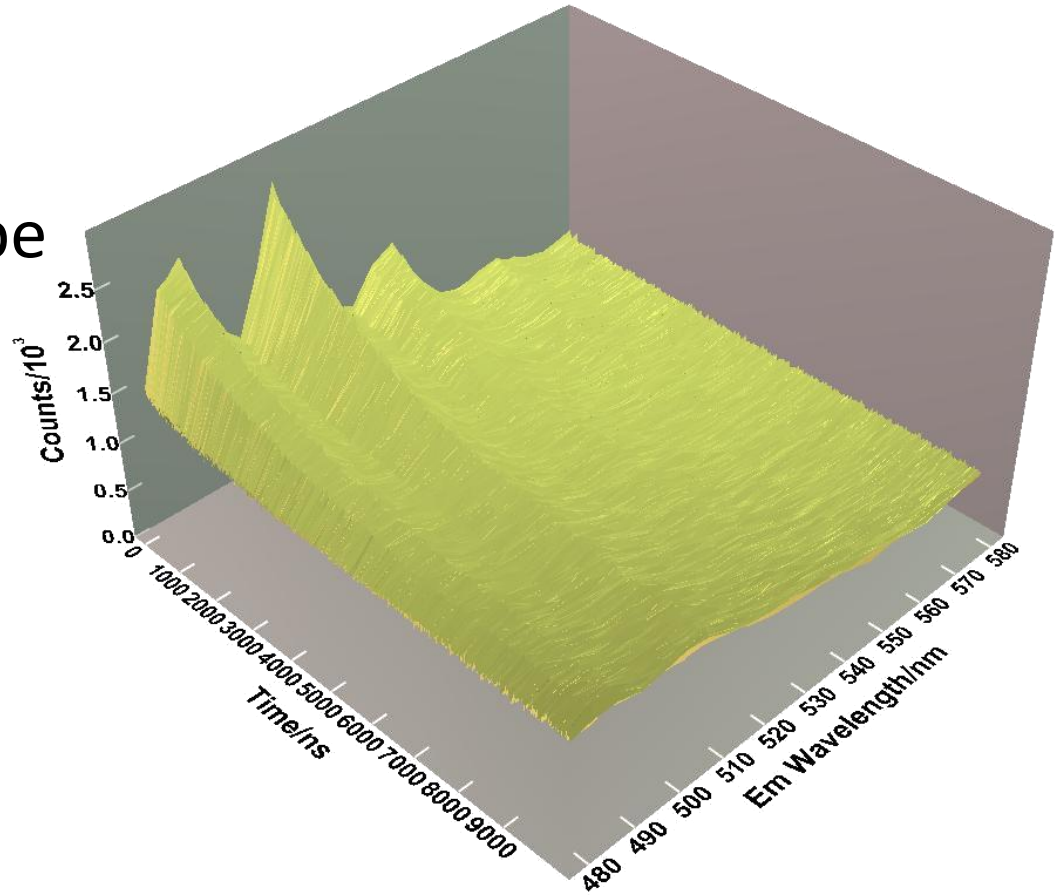
Time resolved mapping

- Uranyl perchlorate $1x10^{-4}$ mol dm^{-3}
- Allows speciation to be determined



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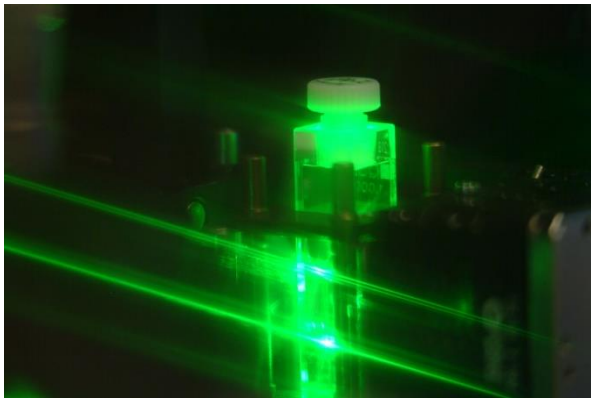
Future Work

- New laser system to be installed and characterised
- Data collection at cryogenic temperatures to be investigated
- Database of certified reference materials to be generated
- Uranium dissolution experiments to be setup



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Summary

- Both spectral an temporal data for uranium species are able to be collected with off the shelf instrumentation
- Relevant environmental concentrations can be accessed
- Solid and liquid samples possible
- New laser system to be established

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Questions

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