Time resolved laser induced fluorescence spectroscopy at FNSPE

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Motivation

- Nuclear systems and fuel cycles are significantly evolving - efficiency of the resources consumption, safety of reactors, waste repository and a resistance towards proliferation
- Different options allowing decreasing waste volume, toxicity and residual heat have to be studied.
  - Among others, recycling minor actinides, particularly americium, is of high interest due to its major contribution to waste long term toxicity and heat power.
- Processes for minor actinides recycling were developed e.g.
  - The recovery of all transuranium elements from the high activity spent fuel dissolution solution
  - or the recovery of Am and Cm together
  - or the separation of Am alone.

Motivation

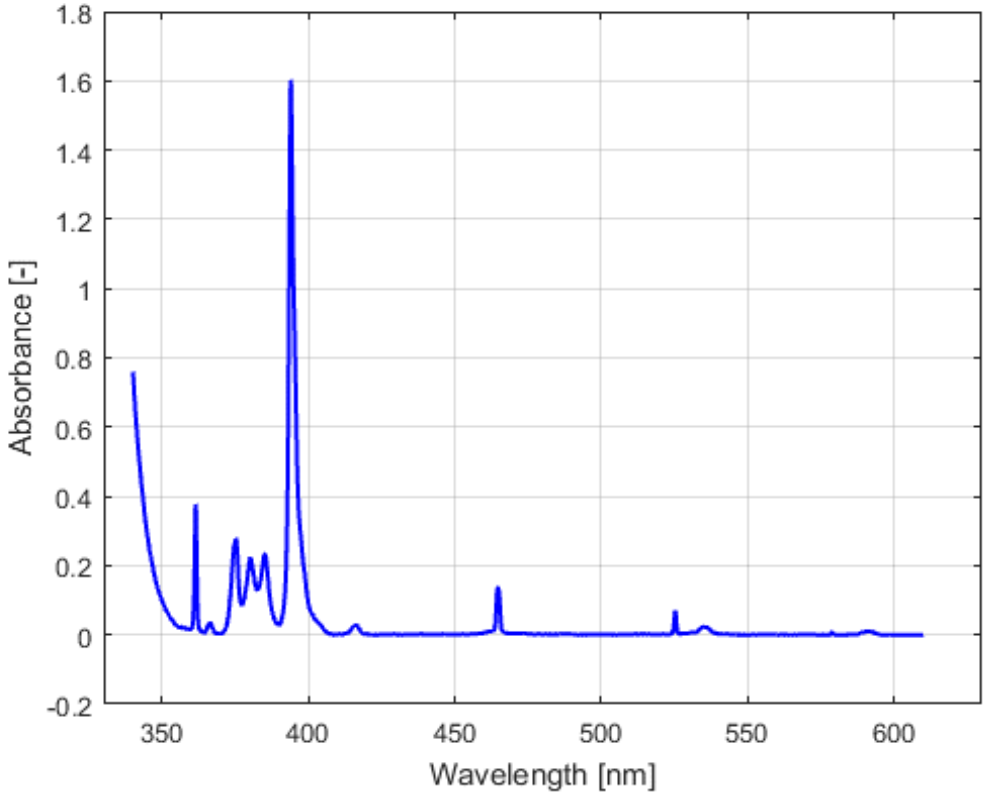
- Different extraction processes based on coordination chemistry were designed for each option, but a representative process modelling needs an description of the structure and the thermodynamics aspects of the systems.
  - Due to the electron configuration Ln and MA are difficult to be distinguish chemically
  - They have different optical properties
  - **Remove chemically, but testing optically**
    - Advantage - Work in small amounts
- Various spectroscopic techniques could provide information; TRLFS could be powerful tool to identify the extracted species and evaluate the effectiveness of the extraction process.
  - Complexation Ln and MA
  - Reaction kinetics
  - Long-term stability of the complex
  - Molecule architecture

Time Resolved Laser Induced Fluorescence Spectroscopy

- Is a modern laser spectroscopic method used for studying chemical forms (species) in which elements are present even in trace concentrations.
- Non-destructive measurements of liquid and solid samples in real time
  - Selectivity
  - Sensitivity (ability to work at concentrations $<10^{-8}$ M and lower)
  - Speed (optional kinetic studies)
- Studied mainly
  - lanthanides **Eu**, Tb, Gd, Dy, Sm, Ce, Tm, Nd, Ho, Er, Yb…
  - actinides **U, Cm, Am**, Cf, Es, Bk**, Np** , Pu…

TRLFS – method principles

- Is based on short-pulse laser excitation of various forms of the studied element and measurement of the luminescence signal characteristics.
  - The sample is irradiated with laser pulses of a selected wavelength - absorption
    - Quantum system (central atom) absorbs a photon enters into the excited state
  - Transition to the ground state follows
    - Non-radiative transitions (very fast) quantum system goes to the lowest excited state. Usually energy transfer direction to the solvent
    - Excited component (complex) emits a photon and system returns to the basic state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1.6
1.4
1.2
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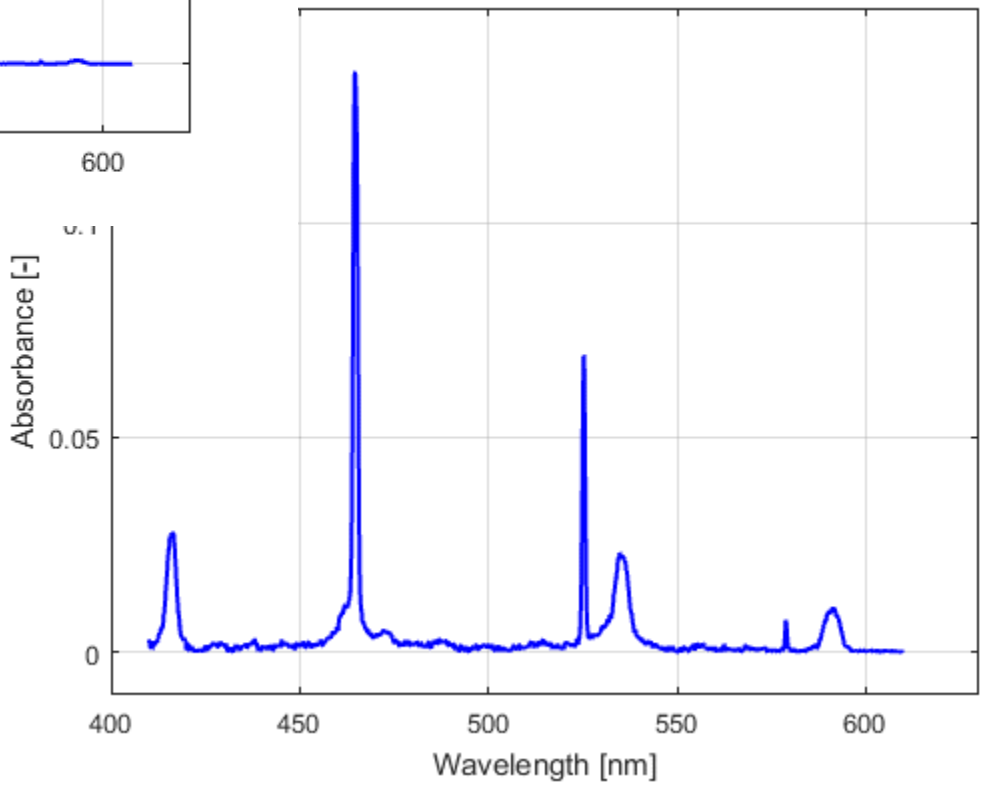
550
600
Wavelength [nm]


Absorbance [-]
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0
400
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500
550
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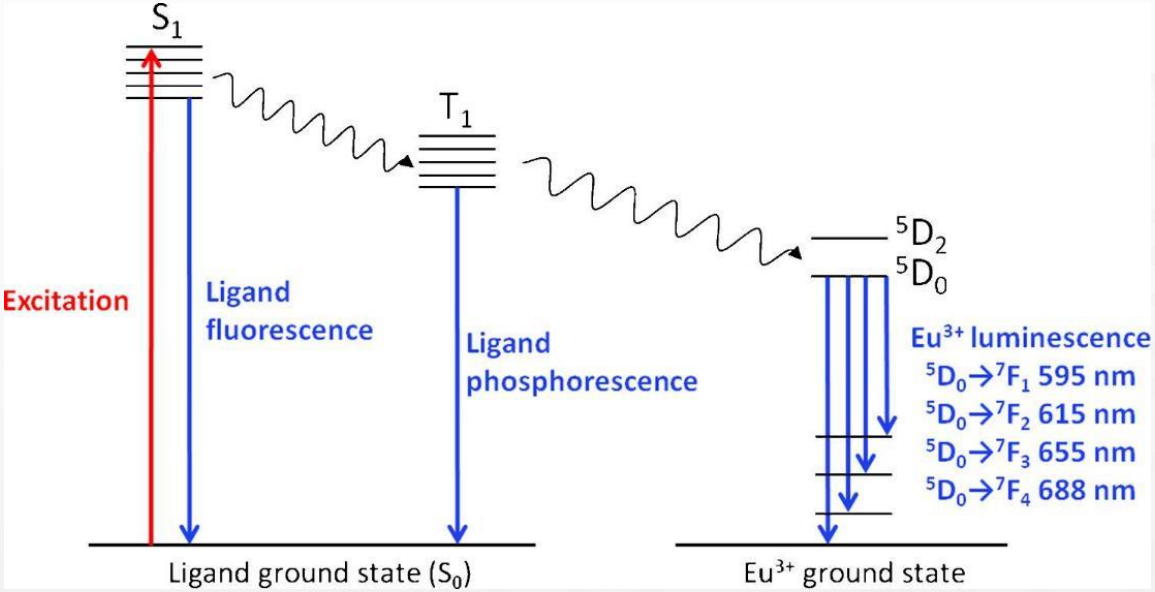
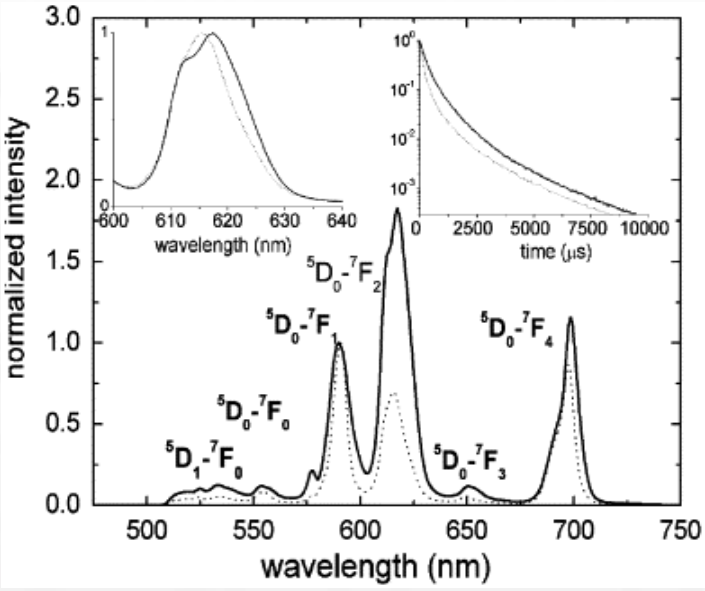
Wavelength [nm]

TRLFS – how to identify

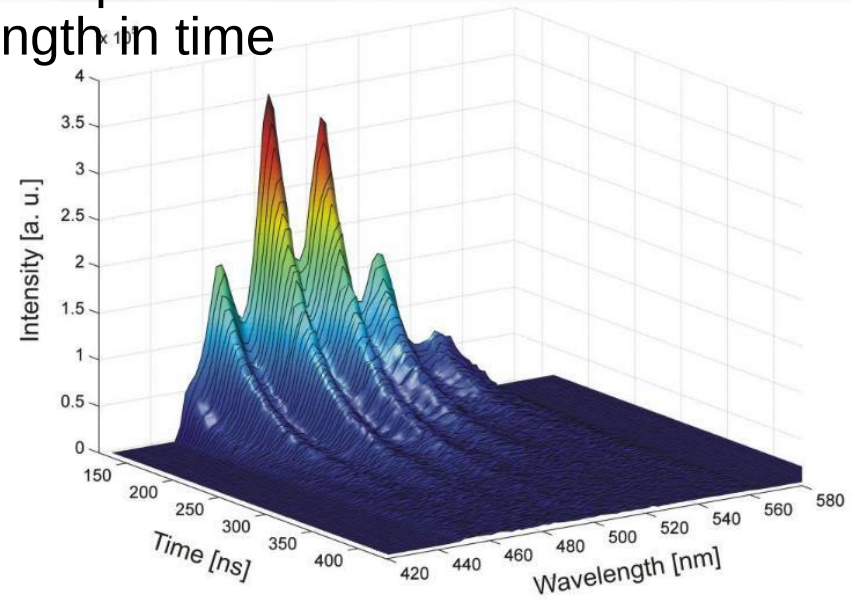
- Following the spectra of emitted wavelengths (spectra shape)
  - Emitted photons are characteristic for the element
  - Spectrum of fluorescence signal is done by a difference of energy levels between which the luminescent transition occurs, depends also on the form (ion, complex, solvated molecule, etc.)



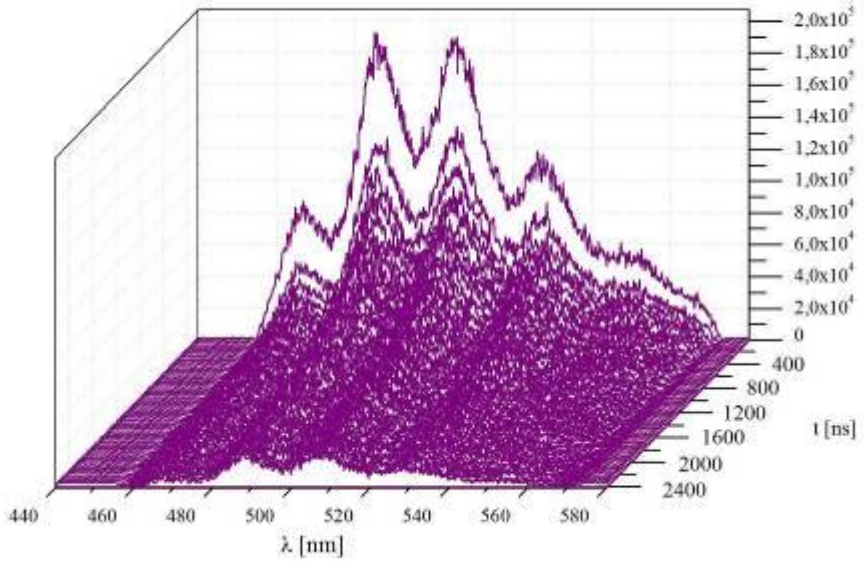


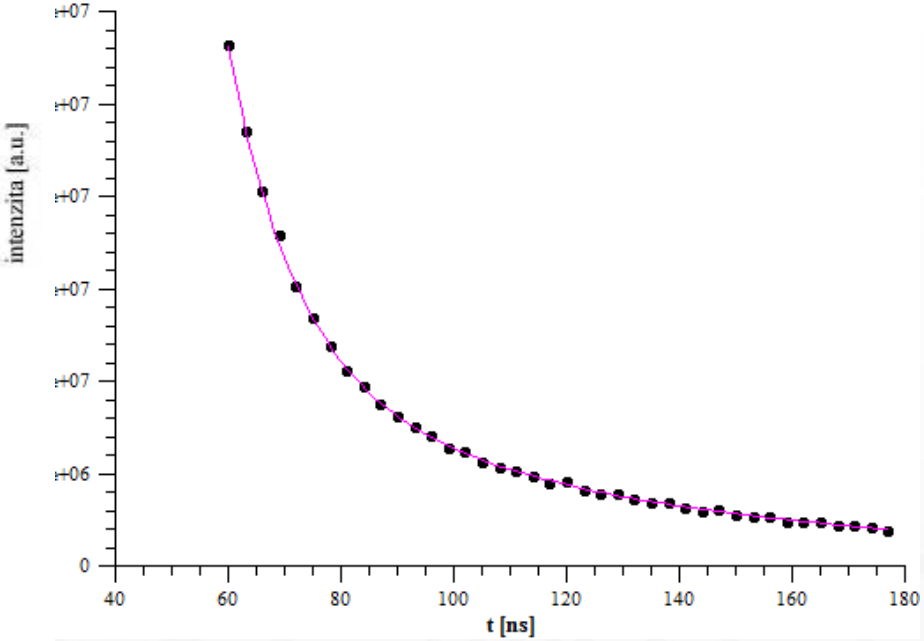
TRLFS – how to identify

- Following the lifetime
  - To each specie correspond a characteristic fluorescence lifetime (radiation intensity drops to 1/e = 36.8% of initial value)
  - The changes in the emission spectra are due to variations in the first coordination sphere of the fluorescent central metal ion and indicate inner-sphere complexation processes.
  - The fluorescence lifetime increases with decreasing number of quenching molecules in the first sphere.
- This creates a 3D spectrum showing the dependence of the intensities of luminescence for the respective wavelength in time
  - Time resolution is achieved by successive delaying of spectra acquisition against the excitation pulse.

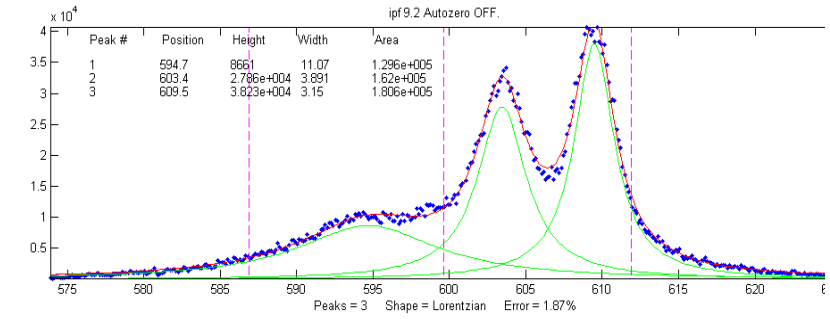


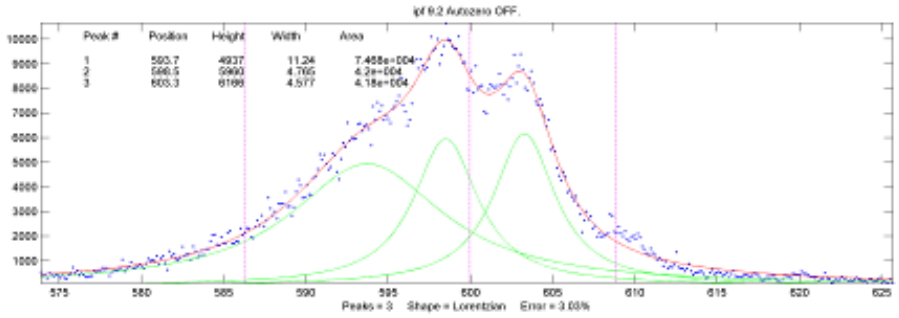
- For each time interval, determine the total fluorescence intensity





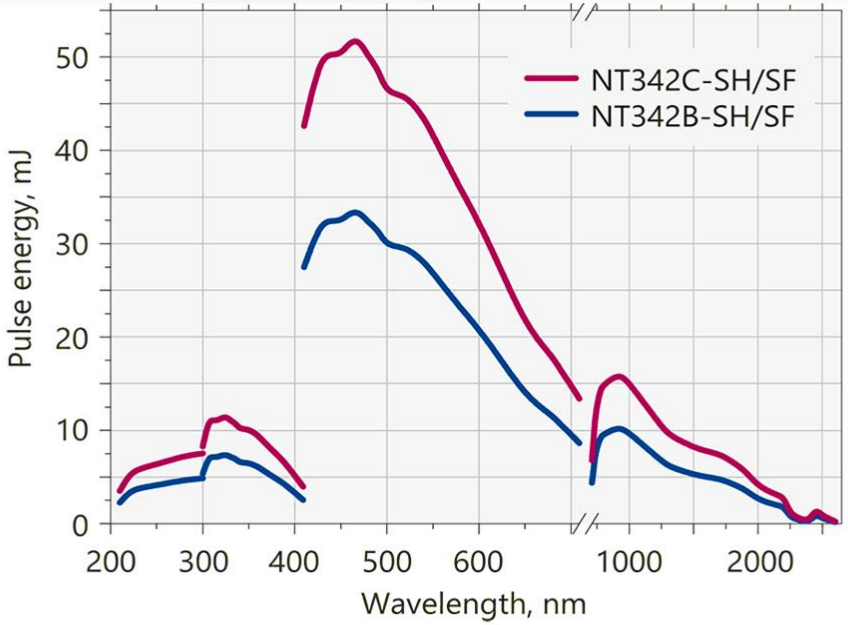
- Specify local maxima and determine the lifetime of a given maximum





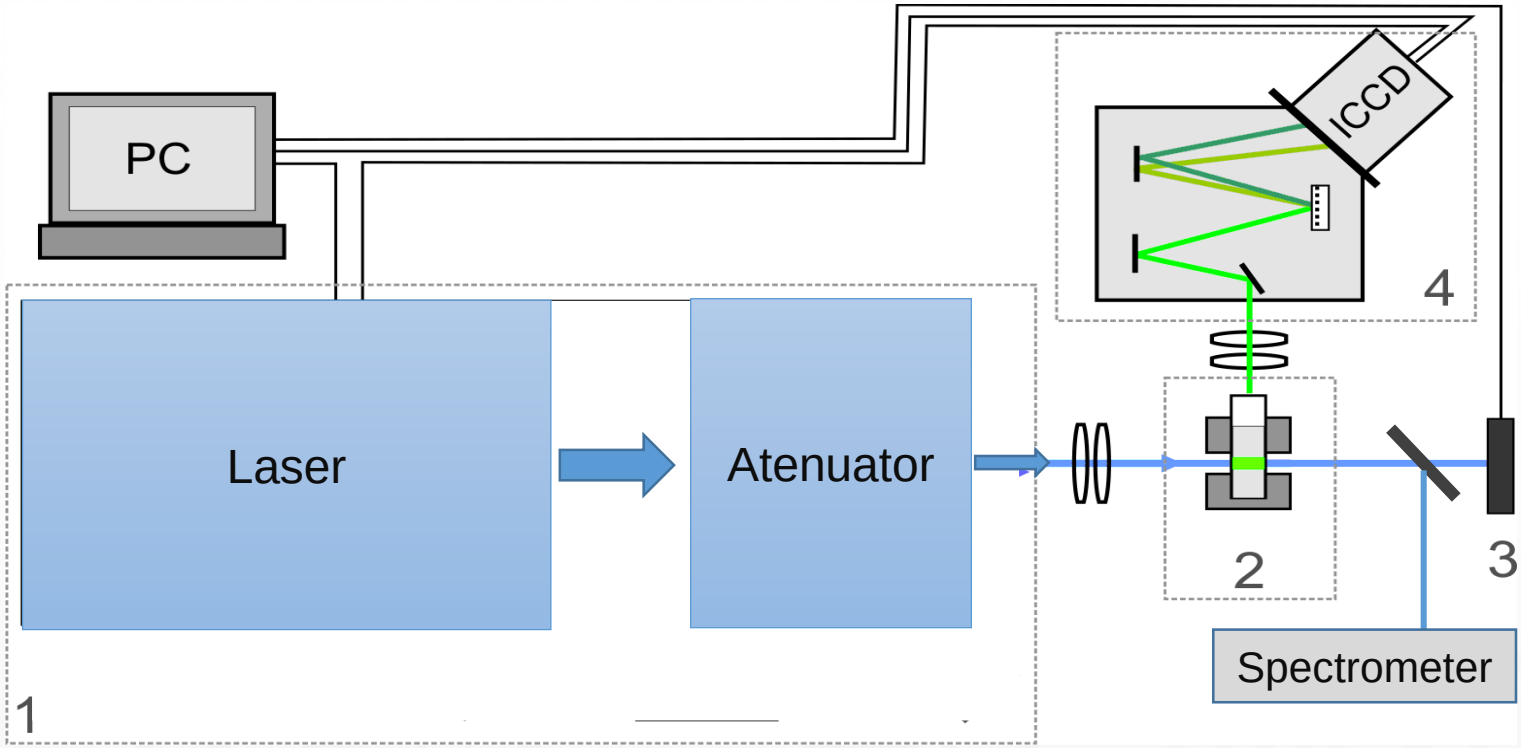
What we have

- **Tunable laser** NT342C Ekspla, OPO based 210-2600 nm
  - Wavelngth range 410-2600 nm, pump on 355 nm Nd:YAG (150 mJ). Signal 410-710 nm, Idler 710-2600 nm
  - Extension in to UV via module SH/SF generator 210-410 nm
  - Output for THG-355 nm and FHG-266 nm.
  - Length of output laser pulse 3-5 ns following the wavelength
- **Attenuator**
  - Made from two Glan polarizers, Beam dumps (to dissipate heat)
  - Attenuation range from 0,1% to ~ 80% in 350-2000 nm



What we have

- **Monochromator/spectrograph** MS257 LOT-Oriel with four gratings(150 l/mm 190-800 nm, 300 l/mm 250-1150 nm, 600 l/mm 280-1200 nm, 1200 l/mm 280-1600 nm).
  - Resolution 0,1 nm
- **Detection part with ICCD** (Intensified Charge Coupled Device) and detection had Andor (DH720i-18F-03), image intensifier (photocatode, MCP (microchannel plate).
  - Gate step 2,4 nm
- **Temperature tuneable cell holder** TC 101 Quantum Northwest, to avoid fluctuation of the temperature-dependent luminiscence signal
- **Joulmeter** Field Max II Coherent with J-50 MB-YAG probe
  - 0,5 mJ - 3 J, 266- 2100 nm
- **Fiber spectrometer** Black comet with Concave Grating
  - measurements in the 190-850 nm range, resolution (<0.4nm)


PC
ICCD
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Laser
Atenuator
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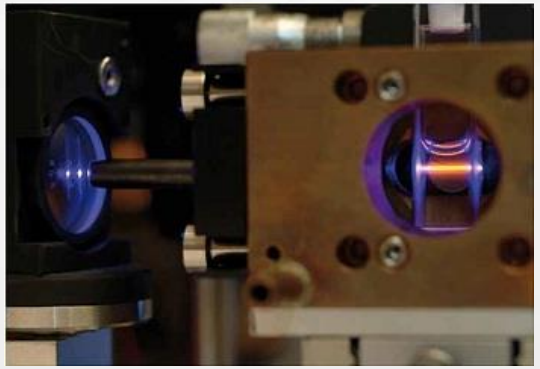
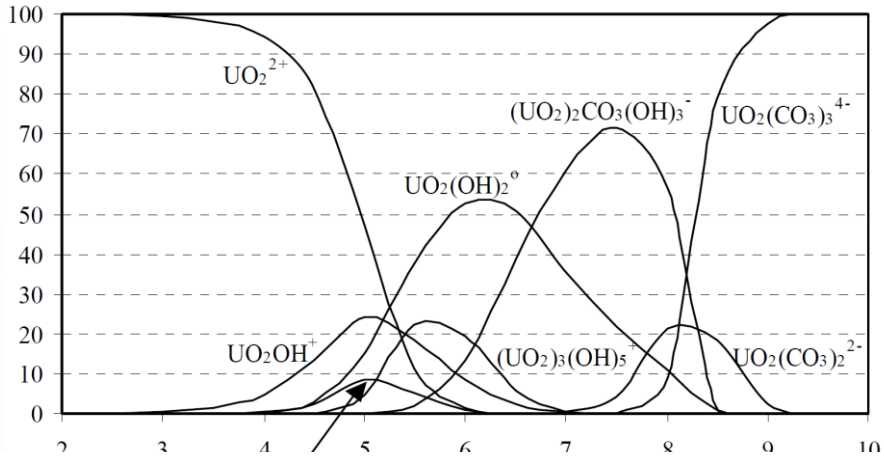
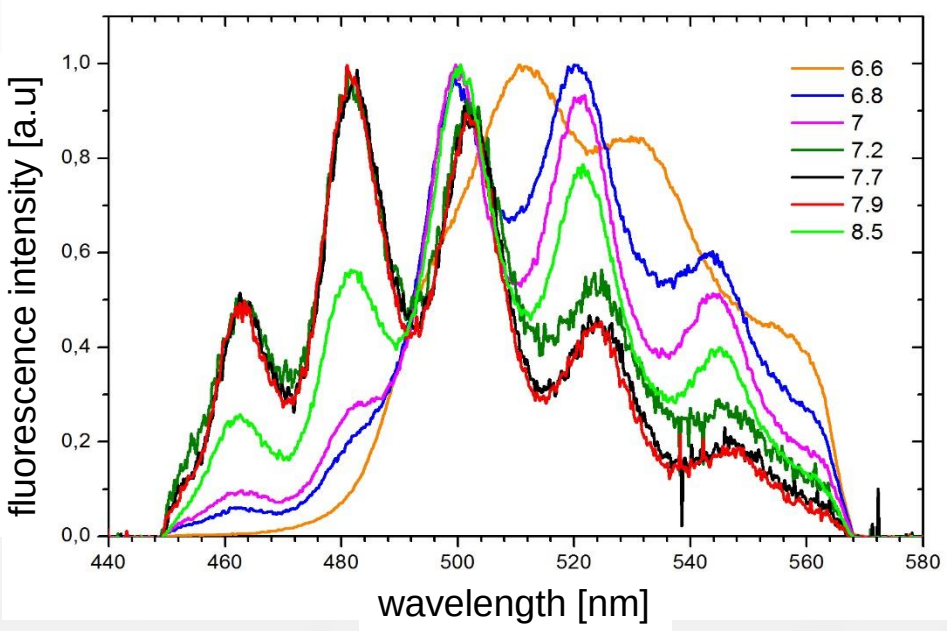
Spectrometer
1



Uranium carbonates results

- Study of behaviour of uranium in the natural environment - species creation is highly dependent on the pH.
- We studied systems in which are present alkaline earth metal – Mg, Ca, Sr and Ba.
- Samples were prepared near its composition of natural samples.
- Formation of species was studied in dependence on the concentration of the alkaline earth metal in solution at a given pH.
- Uranium concentration in all samples was the same 10^{-5} mol/l, the concentration of alkaline earth metal was varied from 2.10^{-2} mol/l to z 6.10^{-3} mol/l.
  Samples were measured at interval of pH ~ 7 to ~ 8.5.



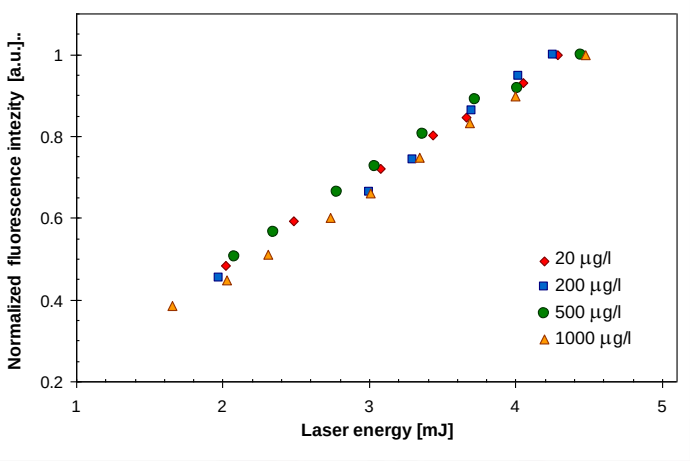


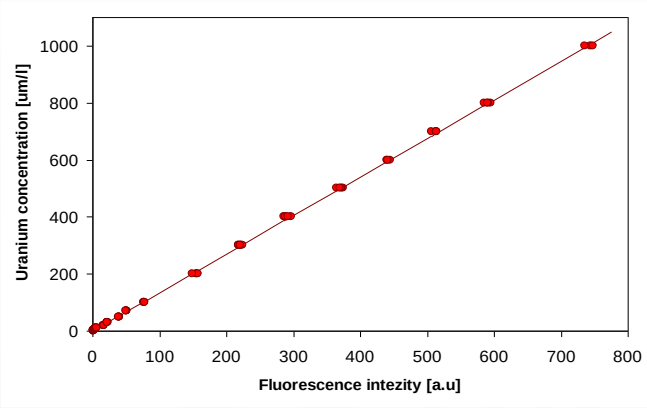
specie	lifetime[ns]	lifetime [ns] (literature)
$UO_2(OH)^+$	6058 ± 1526	11300 ± 4500
$UO_2(OH)_3^-$	313 ± 88	800 ± 100 ; 400
UO_2^{2+}	1718 ± 42	2000 ± 100
$(UO_2)_3(OH)_5^+$	31180 ± 660	33300 ± 5200
$SrUO_2(CO_3)_3^{2-}$	18,4 ± 1,5	18,2 ± 2,1
$Sr_2UO_2(CO_3)_3$	26,2 ± 3,5	28,2 ± 7,1
$(UO_2)_3(OH)_5^+$	27779 ± 5096	33300 ± 5200
$(UO_2)_2CO_3(OH)_3^-$	2243 ± 446	-

c(U(VI)) = 1,00E-05 mol.l^{-1}
c(Ca^{2+}) =7,50E-03 mol.l^{-1}

Uranium concentration measurements

- The linear responses of the uranyl luminescence signal to its concentration at a given intensity of the excitation radiation
- The complexant
  - It serves to reduce the impact of non-irritating processes
  - Reduces the effect of the matrix





- Determination of the amount of uranium in natural waters
  Surface water, mine water, wells, water supply system, Soil contamination
- Barrier proposals
- Testing of ionex function

Matrix effect

- measurement with URAPLEX

added salt,	NaCl		KCl		$CaCl_2$	
conc. ($mol.L^{-1}$)	100 $\mu g.L^{-1}U$	10 $\mu g.L^{-1}U$	100 $\mu g.L^{-1}U$	10 $\mu g.L^{-1}U$	100 $\mu g.L^{-1}U$	10 $\mu g.L^{-1}U$
1×10^{-5}	103.3 ± 0.3	11.3 ± 0.1	102.4 ± 1.5	11.8 ± 1.0	102.5 ± 1.0	11.78 ± 0.02
1×10^{-4}	101.1 ± 1.3	11.8 ± 0.4	103.5 ± 0.1	13.5 ± 2.2	101.1 ± 1.9	10.6 ± 0.5
1×10^{-3}	96.8 ± 0.1	10.0 ± 0.1	98.2 ± 0.3	11.3 ± 0.1	97.5 ± 0.1	10.93 ± 0.01
1×10^{-2}	72.6 ± 3.9	7.7 ± 0.2	74.0 ± 0.8	7.5 ± 0.3	65.0 ± 0.1	6.6 ± 0.1

added salt,	$NaNO_3$		KNO_3		$Ca(NO_3)_2$	
conc. ($mol.L^{-1}$)	100 $\mu g.L^{-1}U$	10 $\mu g.L^{-1}U$	100 $\mu g.L^{-1}U$	10 $\mu g.L^{-1}U$	100 $\mu g.L^{-1}U$	10 $\mu g.L^{-1}U$
1×10^{-5}	101.0 ± 0.5	11.5 ± 0.2	111.4 ± 0.8	10.8 ± 0.3	102.4 ± 0.1	10.7 ± 0.1
1×10^{-4}	116.2 ± 1.0	11.1 ± 0.01	106.0 ± 7.4	12.2 ± 0.1	102.8 ± 1.2	10.5 ± 0.7
1×10^{-3}	109.4 ± 1.4	14.8 ± 0.1	101.6 ± 1.8	11.8 ± 0.2	109.9 ± 1.0	11.7 ± 0.2
1×10^{-2}	105.2 ± 0.8	12.4 ± 0.5	105.0 ± 0.8	12.4 ± 0.2	105.6 ± 1.2	14.5 ± 0.3

Results of europium speciation in the presence of succinic acid

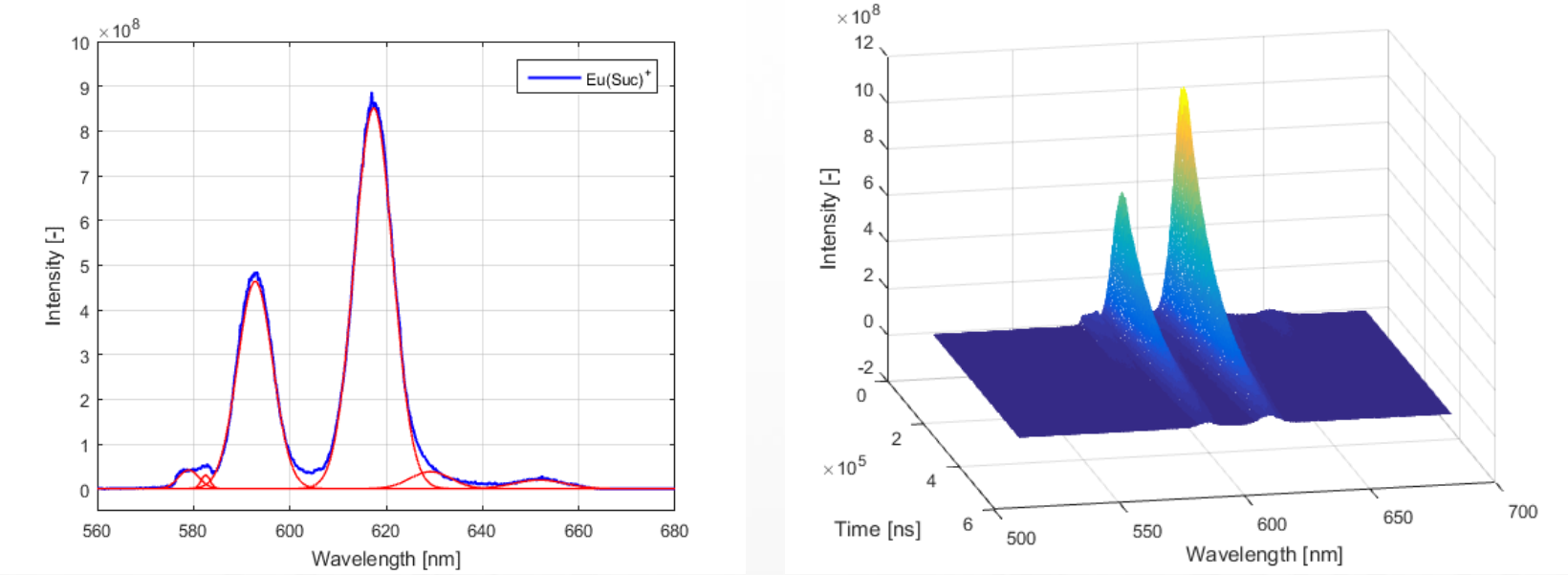


Figure 2: Spectrum deconvolution of $Eu(Suc)^+$ complex (left) and three-dimensional time-resolved luminiscence spectrum of $Eu(Suc)^+$ complex (right).

Results of europium speciation in the presence of succinic acid

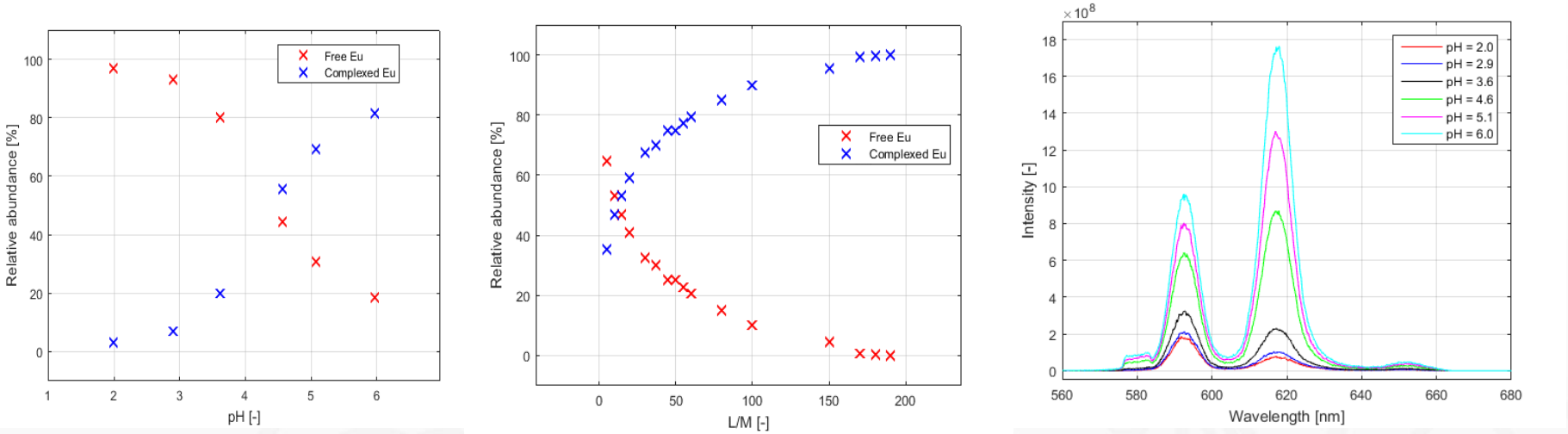


Figure 1: Distribution diagram of Eu in the presence of succinic acid as a function of pH (left), distribution diagram of Eu in the presence of succinic acid as a function of ligand-to-metal ratio (middle) and two-dimensional luminiscence spectra of samples containing Eu and succinic acid as a function of pH.

TRLFS and Am

- Up to now TRLFS studies have been already published with e.g. U(VI), U(IV), Eu(III), Cm(III) and others
- Particularly the europium is often used as a model of fission products from the group of lanthanides and minor actinides.
  - The 5f analog of europium(III) is americium(III).
- Despite the first observation of Am fluorescence emission is more than 25 years old only very few TLRFS investigations of the americium have been performed.
- The interest of Am complexes with TLRFS is limited by the short lifetime of Am (23.4 $\pm$ 1,2 ns in H_2O) which implies a dedicated detection system.
- Absorption of Am ($^5L_6$) **504 $\pm$ 1 nm** (355, 337 nm), emission $^5D_1 \rightarrow {}^7F_1$ (691 nm)

Short fluorescence decay time

- We tested the detection system from point of view
  - of sensitivity especially for weak signal
  - and short fluorescence decay time measurements.
- For a testing system some species of uranium carbonates were selected because of their relatively short fluorescence lifetime at certain condition.
  - $Ca_2UO_2(CO_3)_3$ decay time is 40 ± 5 ns close to the pH ~ 8
  - $SrUO_2(CO_3)_3^{2-}$ is 18,4 ± 1,5 ns close to the pH ~ 8.
  - …
- We were able to measure and calculate the decay times of such species even in this relatively short time scale.
- The speciation study for preliminary measurement were performed.

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Thank you for your attention