



Influence of the speciation of uranium on transfer factors measured by Time-Resolved Laser-induced Fluorescence Spectroscopy (TRLFS)

F. Tawussi, L. Lütke, C. Walther, Institut für Radioökologie und Strahlenschutz,
Leibniz Universität Hannover, Germany (June 2014)

Application Note

Introduction

For the estimation of radiological hazards for humans due to the migration of radionuclides out of a nuclear waste repository, it is necessary to consider the entry of the radionuclides into the food chain. For this purpose it is important to know the transfer factors which describe the radionuclide uptake from soil to plant. The transfer factors depend on various parameters, such as composition of soil, content of minerals, plant species, etc. Another important factor that was often disregarded so far is the influence of the chemical speciation of radionuclides particularly the oxidation state, chemical compound, complexation with organic or inorganic ligands, etc. The Time-resolved Laser-induced Fluorescence Spectroscopy is a very sensitive, non-invasive method to analyze the speciation of complex samples by the fluorescence spectrum and lifetime, especially for uranium(VI) and curium(III) [1].

Experiment

For our present study we investigated the uranium uptake in *Pisum sativum* plants (pea, see fig. 1). The plants were grown in hydroponic Hoagland nutrient solution [2]. The main ions in this solution are K^+ , Ca^{2+} , Mg^{2+} , PO_4^{3-} , NO_3^- , SO_4^{2-} , the pH is about 5.5. The four weeks old plants were incubated in a $25 \mu M$ uranium-containing Hoagland solution for 5 days. To investigate the initial uranium(VI) speciation as an influencing factor on the plant uptake the solution was analyzed by TRLFS before contact with the plants. The uranyl ion in the solution was excited in the UV with a pulsed Nd:YAG laser source (Diva II, Soliton Laser und Messtechnik GmbH) at an emission wavelength of 266 nm, a repetition rate of 20 Hz and a pulse width of 10 ns. The fluorescing light (457.7 nm to 600.0 nm) was detected by a spectrograph (Shamrock SR-303i-A, Andor Technology) with a grating groove density of 300 l/mm combined with an ICCD camera (iStar DH334T18F-A3, Andor Technology), see fig. 2. Using the internal delay generator, the spectrum was recorded time-resolved with delay periods between laser excitation and fluorescence light detection from 50 ns up to a maximum of 3400 ns and with an increment of 10 ns.



Figure 1. *Pisum sativum*, pea plant

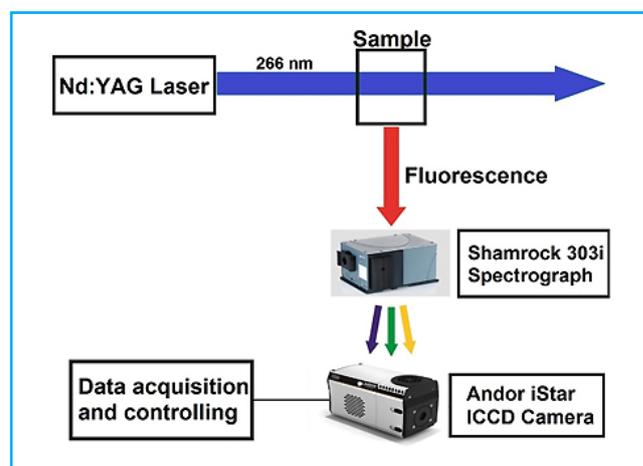


Figure 2. Schematic setup of the TRLFS

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Results

The fluorescence spectrum of the 25 μM uranium Hoagland solution shows fluorescence maxima at 501.5 nm, 522.4 nm, 544.5 nm and 573.3 nm, depicted in fig. 3 for different delay times. The background corrected integrals of the spectra are calculated between 457.7 nm and 600.0 nm and fitted by a monoexponential function giving a lifetime of the species about $\tau = 666 \pm 5$ ns (see fig. 4).

Compared with Geipel et al., the measured uranyl species accords with the metaautinite $[\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 4(\text{H}_2\text{O})]$ in solid suspension (501.8 nm, 522.9 nm, 546.9 nm, 572.2 nm; lifetime: 740 ± 100 ns), [3]. Metaautinite being the major species formed appears to be reasonable because the concentration ratio uranium to phosphate was 1:1. This was also validated by Medusa (species calculation program), [4].

Furthermore, the formation of hydroxide species, such as UO_2OH^+ , is very likely for the chemical conditions. They cause signals with much longer lifetimes around 40,000 ns.

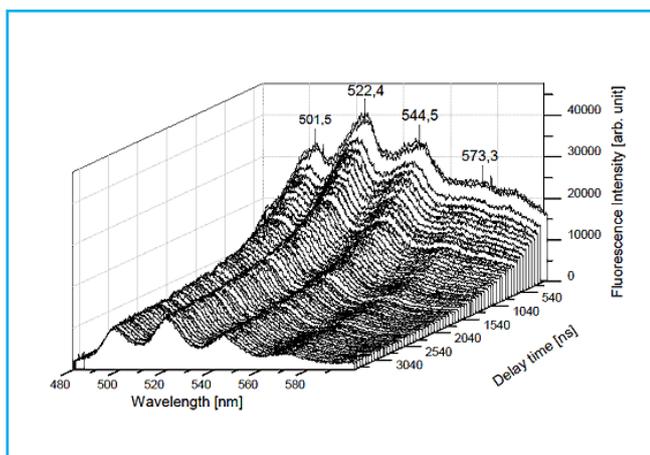


Figure 3. Time-resolved fluorescence spectrum of the 25 μM uranium Hoagland solution

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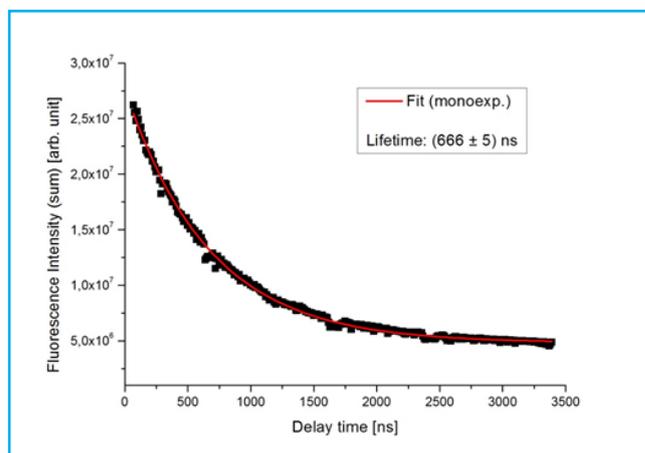


Figure 4. Lifetime graph from the integrated spectra of figure 3 of the 25 μM uranium Hoagland solution

Conclusion

With the ability to obtain time-resolved spectra with the combination of the Shamrock spectrograph and the iStar ICCD camera, information on the chemical compounds uranium forms in solution is accessible. In the current example, TRLFS measurements were appropriate to prove the presence of the metaautinite phase in the micromolar range. Further work will be concerned with the uranium species after plant interaction and the investigation of lower uranium concentration in nanomolar range. For a more sensitive measurement, the setup will be added by a cryostat to cool the samples down and reduce background noise.

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Contact

M.Sc. Frank Tawussi
Dr. Laura Lütke
Institut für Radioökologie und Strahlenschutz (IRS)
Leibniz Universität Hannover
Herrenhäuser Str. 2
30419 Hannover
Germany

Phone: +49 (511) 762 -14326 (Frank Tawussi),
-14325 (Laura Lütke)

E-mail: tawussi@irs.uni-hannover.de,
luetke@irs.uni-hannover.de

Web: www.irs.uni-hannover.de

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