

การตรวจวัดสปีชีส์ของยูเรเนียม (VI) ในแหล่งน้ำธรรมชาติโดยวิธี TRLFS

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บทคัดย่อ

TRLFS (Time-resolved Laser-induced Fluorescence Spectroscopy) เป็นวิธีการที่มีประสิทธิภาพ และมีข้อจำกัดน้อยมากในการวิเคราะห์สปีชีส์ของโลหะหนักบางชนิด เช่น ยูเรเนียม และเป็นวิธีที่เหมาะสมกับการตรวจหาสปีชีส์จากไอออนที่มีปริมาณน้อยในสิ่งแวดล้อม ดังนั้น TRLFS สามารถนำไปใช้ในการประเมินความปลอดภัยในการเคลื่อนที่ของวัสดุกัมมันตรังสีในสิ่งแวดล้อม งานวิจัยนี้ได้ศึกษาการตรวจวิเคราะห์สปีชีส์ของยูเรเนียมในตัวอย่างน้ำที่รั่วซึมตามธรรมชาติและตัวอย่างน้ำในดิน ตัวอย่างน้ำทั้งหมดถูกเก็บมาจากสถานีทดลอง Gessenwiese ใกล้เมือง Ronneburg ในแคว้น Thuringia ตะวันออก ประเทศเยอรมนี สถานีทดลองนี้ถูกใช้ในงานวิจัยของ มหาวิทยาลัย Friedrich Schiller University เมือง Jena เพื่อการตรวจสอบความปลอดภัยทางรังสีในพื้นที่ที่ถูกฟื้นฟูขึ้นใหม่ หลังจากการทำเหมืองแร่ยูเรเนียม การวิเคราะห์ตัวอย่างน้ำที่เก็บมาจาก สถานีทดลอง Gessenwiese โดยเทคนิค TRLFS พบว่าการเกิดสปีชีส์ของยูเรเนียมในน้ำที่รั่วซึมถูกควบคุมโดยมอนอเมอร์ของยูเรเนียม (VI) ที่ผ่านการทำปฏิกิริยากับน้ำในรูป $UO_2SO_4(aq)$ ผลลัพธ์ที่ได้เป็นการยืนยันว่าเทคนิค TRLFS นี้เป็นวิธีที่เหมาะสมในการวิเคราะห์สปีชีส์ของยูเรเนียมในตัวอย่างจากแหล่งน้ำธรรมชาติ ที่มี pH อยู่ในช่วง 3.2-4.0

คำสำคัญ: ยูเรเนียม สิ่งแวดล้อม TRLFS การประเมินความปลอดภัย

Uranium (VI) Speciation in Natural Waters Determined by TRLFS

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Abstract

Time-resolved Laser-induced Fluorescence Spectroscopy (TRLFS) is a very helpful tool with an extremely low detection limit for analyzing speciation of certain radioactive heavy metal ions like uranium (VI). Thus this technique is preferential appropriate for detection of speciation from that ions in environmental relevant concentrations. So TRLFS can be useful in safety assessment concerning migration behaviour of radioactive elements. In this study, the uranium speciation in natural occurring seepage water samples, and in soil water samples, all samples collected from test site "Gessenwiese" close to Ronneburg in Eastern Thuringia (Germany), were analyzed by TRLFS. This test site was

installed as a part of a research program of the Friedrich Schiller University at Jena for investigations within the area of recultivated former uranium mining heaps. The TRLFS measurements on water samples collected within test site Gessenwiese revealed that the uranium speciation in that seepage water is dominated by the hydrolyzed and monomer uranium (VI) sulfate species $\text{UO}_2\text{SO}_{4(\text{aq})}$. The results presented here are a convincing example for the suitability of TRLFS in analyzing the speciation of uranium from natural occurring water samples with pH values between 3.2 and 4.0.

Keywords: uranium, environment, TRLFS, safety assessment

1. Introduction

There are lots of ecological problems followed from extreme inconsiderate uranium mining in Eastern Germany between 1945 and 1989. To countervail these problems knowledge about speciation of radio nuclides is necessary, because speciation influence there transport and migration. Most important radioactive elements in that region are radium and uranium. The aim of this contribution presented here is to identify the speciation of uranium in seepage and pore water of the “Gessenwiese” environment, a recultivated former uranium mining heap in Thuringia (Germany). Uranium is a potentially dangerous element, which in enriched concentrations represents a health hazard. Uranium transport behavior depends on its oxidation state. In contrast to tetravalent uranium, U(VI) is more soluble and may migrate in the environment via water path.

The method of Time-resolved Laser-induced Fluorescence Spectrometry (TRLFS) combines low detection limits and a high sensitivity toward U(VI) complex formation in aqueous solutions. Elemental uranium does not emit fluorescence^{1,2}, whereas U(VI) emit characteristic fluorescence signals and are thus detectable with TRLFS. Aqueous complexes of hexavalent uranium have been well investigated as also solid uranium(VI) phases³ and uranium(VI) species adsorbed on mineral surfaces^{4,5}. In this study TRLFS was used to identify the uranium speciation in natural seepage water and soil water, because speciation determines chemical reactivity and thus its transport behaviour and bio-availability.

2. Method

2.1 Sampling campaign

The surface water samples SrfWtr1 and SrfWtr2 were collected in and close to the test site Gessenwiese (Fig. 1) from a little creek in the north. Soil (pore) water samples (SoilWtr1-3) were extracted from Gessenwiese soil (30 to 100 cm depth) of the site section MF 3 (Fig. 1).

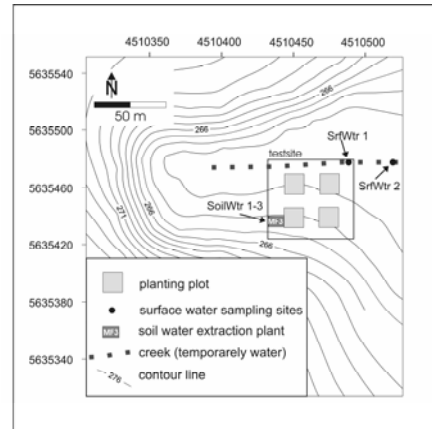
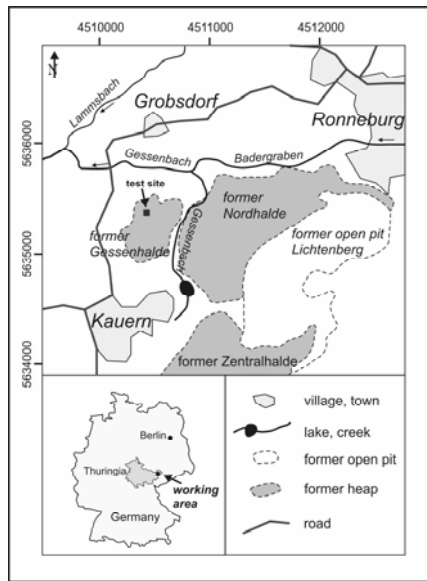


Fig. 1 Test site Gessenwiese near Ronneburg in eastern Thuringia (left) with test field and sampling sites (above). Coordinates: German grid (Gauß-Krüger zone 4).

2.2 Water analyses

All water samples investigated in this study show a pH between 3 and 4, and contain high concentration of heavy metals, including uranium, and a high concentration of sulfate. Chemical composition of seepage water samples and soil water samples were analyzed for cations by inductively coupled plasma mass spectrometry (graphite furnace atomic absorption spectrometry for Fe). Anions were determined by ion chromatography. Results can be provided by the author.

2.3 Description of the TRLFS analyses

The TRLFS system contains a Nd:YAG diode laser, excitation wavelength was 266 nm. The resulting generated fluorescence signal was collected perpendicular to the excitation beam and focused into a fibre optic cable that was coupled to the slit of a triple-grating spectrograph.

3. Results and Discussions

TRLFS-results on U(VI) species on natural surface water samples and natural occurring soil water samples - not on samples synthesized in the laboratory - were presented.

3.1 Surface water samples

These samples provided an evaluable fluorescence signal for TRLFS; one example of a time-resolved fluorescence signal is shown in Fig. 2. The positions of the peak maxima from these signals in both water samples are shown in Table 1 and are in agreement with data for uranium sulfate species

published in the literature⁶. The TRLFS-signals of both water samples possess a mono-exponential decay, indicating the presence of only one main species. These two characteristics, i.e. positions of peak maxima and lifetimes revealed without doubt that the uranium speciation in the seepage water is dominated by the uranium (VI) sulfate species $\text{UO}_2\text{SO}_{4(\text{aq})}$. A mono-exponential decay curve from sample SrfWtr1 is shown in Fig. 2 (right).

Table 1 Positions of the peak maxima of the fluorescence signals from SrfWtr1 and SrfWtr2 in nm, rounded in whole nm, and lifetime of the signals t in μs .

	1 st peak	2 nd peak	3 rd peak	4 th peak	5 th peak	6 th peak	t
SrfWtr1	477	491	513	537	562	591	1.6
SrfWtr2	478	492	513	538	562	590	1.0

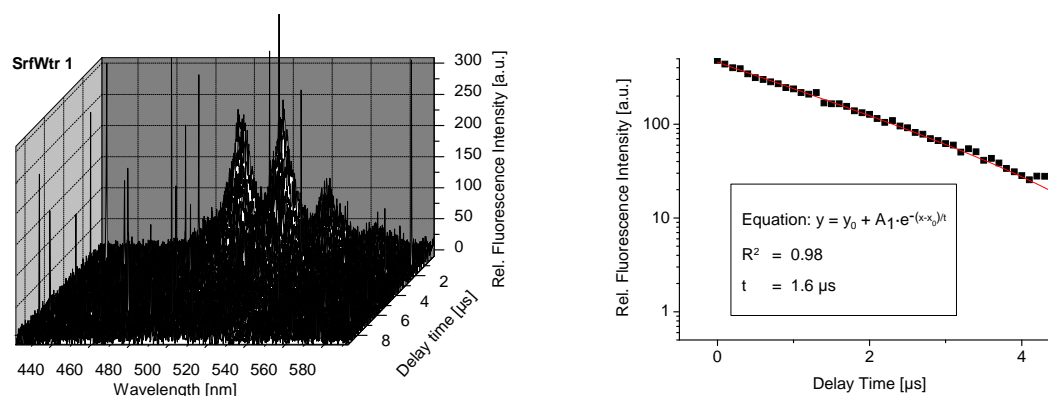


Fig. 2 Time-resolved laser-induced fluorescence signal obtained from sample SrfWtr1 (left) and life time curve from the fluorescence signal sample SrfWtr1 (right).

3.2 Pore water samples

All three pore water samples from the test field showed an evaluable fluorescence signal for TRLFS too. The three spectra with the highest fluorescence intensity of the soil water samples are shown in Fig. 3 and the emission maxima and fluorescence lifetimes are shown in Table 2.

Table 2 Positions of the peak maxima from the fluorescence signals of three soil (pore) water samples in nm, rounded in whole nm, and lifetime of the signals t in μs .

	1 st peak	2 nd pak	3 rd peak	4 th peak	5 th peak	6 th peak	t
SoilWtr1	480	492	514	537	562	590	2.6
SoilWtr2	473	492	513	535	562		1.7
SoilWtr3	477	493	514	538	562	590	1.0

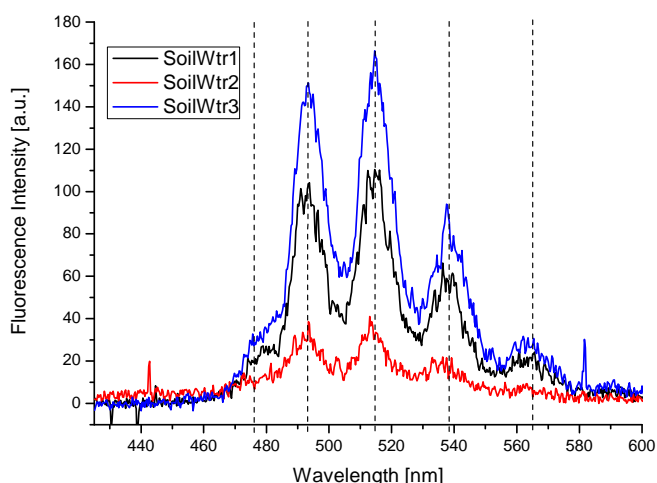


Fig. 3 Intensity from the fluorescence signals of the three pore water samples, in comparison with positions of peak maxima published in literature for $\text{UO}_2\text{SO}_{4(\text{aq})}$ (dashed lines).

4. Conclusion

It was shown that TRFLS is a useful tool for identifying the speciation of uranium in natural waters characterized by low pH and high metal concentrations. Uranium speciation in natural occurring seepage water samples, and soil water samples, all samples from test site Gessenwiese in Thuringia (Germany), were analyzed by TRFLS. The positions of the six peak maxima from these signals are in all five water samples in agreement with data for uranium sulfate species $\text{UO}_2\text{SO}_{4(\text{aq})}$. Moreover, the TRFLS-signals of all five water samples possess a mono-exponential decay, indicating the presence of only one main uranium species. These two characteristics, i.e. positions of peak maxima and the observed mono-exponential decay of the fluorescence signal revealed that the uranium speciation in the seepage water is dominated by the uranium (VI) sulfate species $\text{UO}_2\text{SO}_{4(\text{aq})}$. The analyses were performed to compare the results on the identified uranium speciation in a later stage with the uranium speciation in plants, which grow on the grassland test site Gessenwiese and take up the same uranium contaminated water during their growth. TRFLS measurements with plant compartments which grow in association with the seepage water will be carried out within future investigations, and will be compared to the identified uranium speciation in surface water and soil water of the Gessenwiese presented here, because reactivity and toxicity of uranium depend on its speciation, and has to be considered as important possible risk factor as uranium may enter economic plants and eventually arrives in the food chain.

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6. References

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