Spectroscopy of f-elements in the Near Infrared Region

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Application Note

Introduction

The Institute of Resource ecology is involved in studies of the behavior of actinide elements in the environment. Especially the migration of these elements in a radioactive waste disposal is a main research complex in the institute. Despite this also studies on the behavior during the transition from geosphere to biosphere were performed. In this topic are interactions with microorganism, as can be found in the waste disposal, as well as the uptake by plants and herewith the distribution with the food chain of enormous importance.

Some of these elements like uranium, americium and curium show powerful fluorescence properties, which can be used for speciation studies as well as to obtain information about the structure of these compounds. In case of trivalent actinides also lanthanides are used as non-radioactive substitution.

To study neptunium and plutonium other methods to get this information have to be used. However, in the literature [1,2] one can find that neptunium in the oxidation state +6 should show also fluorescence properties. Additionally neodymium has some strong emissions in the NIR region.

Setup

Basis of the setup is an arrangement, how it is used also for time-resolved laser-induced fluorescence spectroscopy (fig.1).

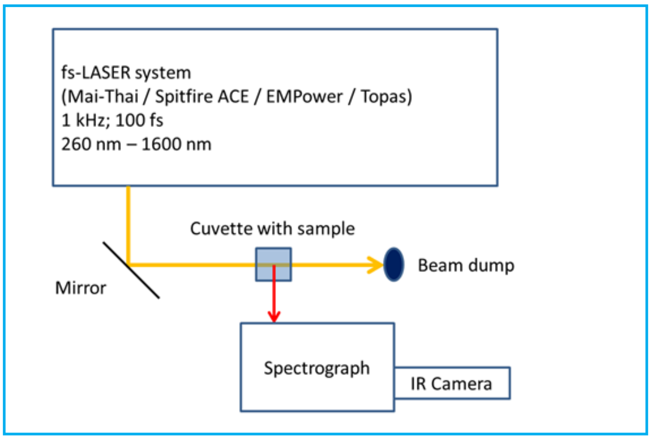

Fig. 1 Principal scheme of the Fluorimeter

A pulsed, tunable laser system is used as excitation source. As about the fluorescence of Np(VI) up to now can be found in the literature only two publication [1, 2] we used a tunable femto second laser system (Newport-Spectra-Physics). This laser system provides pulses with duration of 100 fs and a repetition rate of 1 kHz. The excitation wavelength can be freely selected in a range from 260 nm to 1600 nm. The laser pulse is directed towards the sample, in our case a broken Nd:YAG rod or a solution in a standard cuvette. The emitted fluorescence radiation is focused into the spectrograph (Shamrock SR-303i-A, 2 gratings 150 l/mm and 300l/mm; LOT-QD) in a right angle setup. In the spectrograph the spectral distribution is generated. The assembled IR-camera (iDus InGaAs DU490A-2,2, 512 pixels; LOT-QD) measures the spectra. A photo of the setup is shown in Fig. 2.

Fig. 2 Photo taken of the actual setup in the laboratory (in the foreground and right the laser excitation source, left from the light source spectrograph and camera system)

Results

To test the setup we measured at first a sample containing 200 nm colloids is aqueous solution. The laser wavelength was set to 600 nm. With this we could measure the direct stray light as well as the second and third harmonic generated at the grating in the spectrograph. Taking into account that on the one hand the second and third harmonic transformation generates less light with increasing harmonic number and on the other hand that the efficiency of the setup has its maximum in the IR region, it was of interest how the measured intensity changes. Nevertheless, it was expected that the measurement of the 600 nm stray light is very inefficient (Fig. 3). The high intensity of the laser pulses generates a very intense signal. The second order of the scattered light is much less intense.

However, due to the optimized efficiency of the grating at 2000 nm the third order is much better. A second test with fluorophores was also planned. However there are no fluorophores available which emit in the spectral region above 1000 nm [3].

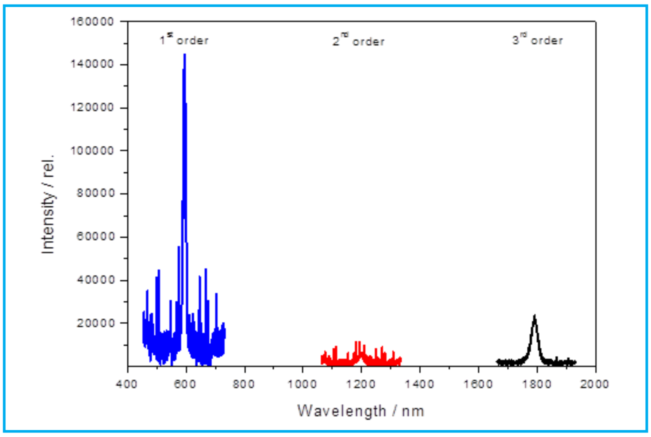

Fig. 3 Measured light scatter of the 600 nm laser pulse

In order to get information about the general suitability of the setup for measurements of emitted radiation in the NIR region we measured a broken Nd-YAG rod from an old lasersystem. The laser was set to an excitation wavelength of 800 nm. As the region of interest between 1000nm and 2000 nm cannot be covered with one measurement up to 6 measurements have been done where consecutive wavelength ranges have been assembled. The result is shown in Fig. 4. The several ranges are marked with different colors.

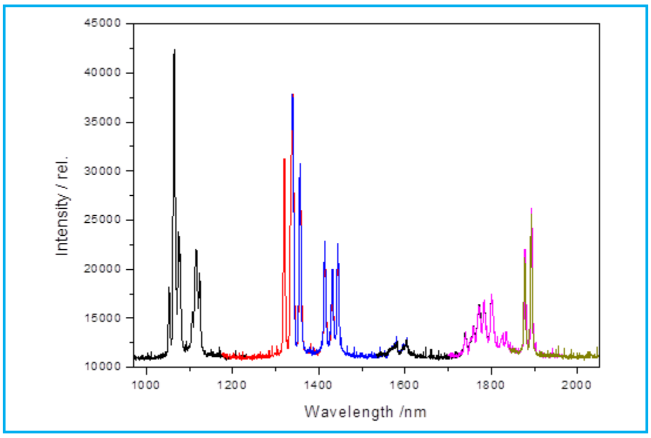

Fig. 4 NIR emission spectrum of a broken Nd-YAG rod

The wavelength range for each measurement covers about 200 nm. As the spectra also have some overlap, it can be also stated that the intensities in the range of overlap agree very well. This underlines that the efficiency of the IR-camera system shows a very good linearity.

In a next step we want to apply this system to measure the fluorescence of neptunium Neptunium(VI) has a strong absorption at about 1223 nm. The molar extinction coefficient has been determined to be 45 L/mol.cm. Nevertheless, in the literature an excitation wavelength of 633 nm is described. From literature [2] a fluorescence signal in the region from 1350 to 1670 nm was detected for a solid phase system. In a second publication [4] a different behavior is described for a deuterated solution. The authors excited their samples at 337 nm and observed the fluorescence of the Np(VI) at 1490 nm and 1580 nm. The lifetime of the fluorescence was determined to be about 10 ns. This is a very short lifetime and probably we have to transfer the neptunium into a deuterated solution.

References

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[3] The Molecular Probes Handbook, Eds. I. Johnson and M. Spence, 11th edition, Life Technologies Corporation, 2010

[4] C. Talbot-Eeckelears et al. (2008) J. Am. Chem. Soc. 129, 2442-2443.

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