

## TIME-RESOLVED LASER-INDUCED FLUORESCENCE IN THE NUCLEAR FUEL CYCLE

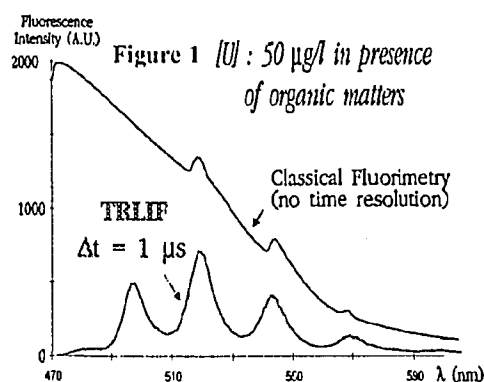
Christophe MOULIN\*, Pierre DECAMBOX, Patrick MAUCHIEN, Alain PETIT  
CEA/DCC/DPE/SPEA/SPS/Analytical Laser Spectroscopy Laboratory.  
91191 Gif sur Yvette cedex, FRANCE

Time-Resolved Laser-Induced Fluorescence (TRLIF) is a very sensitive and selective method that has been used for actinides and lanthanides analysis in the nuclear fuel cycle. This technique has been used in different fields such as in geology, in the Purex process, in the environment, in the medical and in waste storage assessment. Spectroscopic data, limits of detection and results obtained in previously quoted fields are presented.

Keywords : Actinides, Analysis, Fluorescence, Lanthanides, Laser, Time-resolved.

### 1. INTRODUCTION

Fast and sensitive methods are still required in the nuclear fuel cycle for ultratrace determinations of actinides and lanthanides. Time-Resolved Laser-Induced Fluorescence (TRLIF) is a method of choice for such determinations and has been used for now more than 10 years at the CEA. The principle of this technique consists in pulsed laser excitation followed by temporal resolution of the fluorescence signal which leads to the elimination of unwanted short lifetime fluorescence (organic matters, Raman) as seen on figure 1. The main advantage of TRLIF aside rapidity (few minutes analysis) and sensitivity (LoD in the ng/l range) is its triple selectivity : excitation selectivity by the proper choice of the laser excitation wavelength, emission selectivity since each fluorescent element gives a characteristic fluorescence spectrum and finally time resolution selectivity which characterizes the fluorescent element environment. Among the actinides and lanthanides, the ones that are fluorescent in solution are U(VI), Cm(III), Am(III) and Eu(III), Tb(III), Dy(III), Sm(III), Gd(III), Ce(III), Tm(III). These elements have been studied in different complexing media (nitric, phosphoric, sulphuric, carbonate, micellar) and analysed from the part per billion ( $10^{-6}$  g/l) to the part per trillion ( $10^{-9}$  g/l) level and lower [1-6].



The different fields of interest in the nuclear fuel cycle where TRLIF has been used are in :

- Geology, for ultratrace determination of uranium (ng/l level) in waters from different localities in order to obtain a better understanding of uranium mobilization under natural reducing conditions and so to validate thermodynamic data [5];
- Environment, for uranium determination in water and soil samples in order to have a "cartography" of specific areas as well as speciation with the use of micellar enhanced ultrafiltration [7-9];
- All the different steps of the Purex process, in very complex matrices (Pu, Na, fission products) and for direct speciation in nitric acid [10-12];
- Medical surveillance for direct and fast determination of uranium in human urines. Hence, based on the uranium concentration in urine, metabolic models are established to estimate the body burden of uranium from persons exposed to uranium ambience [13] ;
- Waste storage assessment, for the determination of complexing constants at very low level between actinides and organic matters. TRLIF allows to work directly at trace level and has been applied to curium, dysprosium and uranium [14-16].

Moreover, in Purex process control, remote TRLIF measurements are performed in gloves-box or shielded cell with the adaptation of fiber optics and optode [17] and is foreseen for environmental purposes [18].

## 2. MATERIAL AND METHODS

*Apparatus* : The experimental set-up is schematically shown in Figure 2.

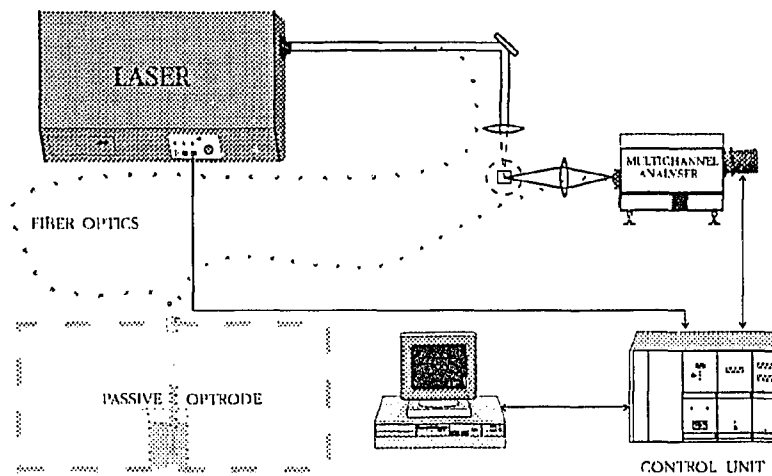


Figure 2 : TRLIF experimental set-up (dotted lines for remote TRLIF).

A laser ( $N_2$  (337 nm), excimer (308 nm) or Nd-YAG (355 nm)) coupled or not with a dye laser is used as excitation source. The laser beam is focused into the cell of the spectrofluorometer "FLUO 2001" (DILOR, 244 rue des Bois Blancs, 59000 Lille, France) by a quartz lens. The radiation coming from the cell is focused on the entrance slit of the

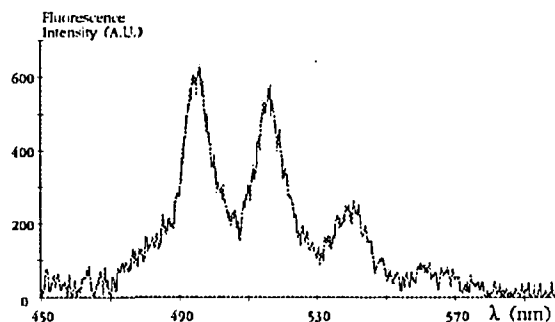


Figure 3 : Fluorescence spectrum of uranium at 0.5 ng/l in phosphoric acid (0.75M)

TRLIF coupled with Micellar Enhanced UltraFiltration (MEUF) is used for uranium speciation in the environment. Hence, MEUF allows charge selectivity (affinity with the charged micelle surface) as well as size discrimination to a less extent as schematically shown on figure 4. With such features, it is possible to separate the different species present in solution and to perform speciation at very low level.

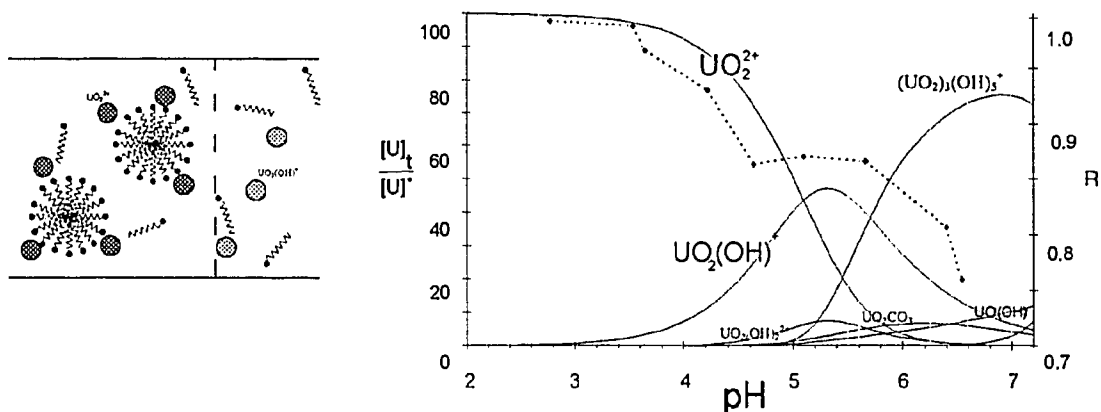


Figure 4 : Schematic of MEUF and speciation of uranium in solution.

Dotted line represents experimental data.  $[U] = 1 \text{ mg/l}$ .

*In the Purex process* in the presence of plutonium, americium, neptunium, fission products, sodium, organic effluents (for example in the TEO (Organic Waste Treatment) in order to determine the decontamination factor (DF) by using uranium as tracer in the organic phase (TBP; TPH)), directly in nitric acid to avoid the use of complexing reagents (such as  $\text{H}_3\text{PO}_4$ ) which generate effluent. This last step allows also to perform direct uranium speciation in nitric acid since the different uranium-nitric acid complexes ( $\text{UO}_2\text{NO}_3^+$ ,  $\text{UO}_2(\text{NO}_3)_2$ ) affect fluorescence spectrum (figure 5). This spectral modification permits spectral deconvolution and the determination of free nitrate in solution.

monochromator (range covered 200 nm). The detection is performed by an intensified photodiodes (1024) array cooled by Peltier effect and positioned at the monochromator exit. Recording of spectra is performed by integration of the pulsed light signal given by the intensifier. The integration time adjustable from 0.3 to 90 s allows for variation in detection sensitivity. Time-resolution is obtained by the control unit that assures pulsed running of the intensifier and the photodiodes array. Measurements are adjustable with a delay from 0.1 to 999  $\mu$ s during a time of 1 to 99  $\mu$ s. All functions of the apparatus (temporal delay, gate width, integration time, reading of spectra, ...) are controlled by a PC-AT microcomputer. Analytical software automatically calculates concentrations by the standard addition or the initial fluorescence methods.

### 3. PERFORMANCES

Table 1 presents convenient excitation and main emission wavelengths, lifetimes and limits of detection (in best complexing media) used in TRLIF for actinides and lanthanides determination in solution.

ELEMENT	$\lambda_{\text{excitation}}$ (nm)	$\lambda_{\text{fluorescence}}$ (nm)	Lifetime ( $\mu$ s) / medium	Limit of detection ( $\mu$ g/l)
URANIUM	337, 420	494-516-545-565	200 / H <sub>3</sub> PO <sub>4</sub>	<b>0.0001</b>
CURIUM	337, 385	612	200 / TTA	<b>0.0001</b>
AMERICIUM	507	697	0.03 / K <sub>2</sub> CO <sub>3</sub>	<b>1</b>
EUROPIUM	337, 394	590-617-650-690	900 / TTA	<b>0.001</b>
SAMARIUM	337, 355, 380	565-600-650-710	80 / TTA	<b>0.01</b>
TERBIUM	337, 355, 380	490-545-590-625	2100 / EDTA	<b>0.1</b>
DYSPROSIUM	355, 390	485-580-670	20 / EDTA	<b>0.01</b>
CERIUM	260	360	0.07 / H <sub>2</sub> SO <sub>4</sub>	<b>0.2</b>
GADOLINIUM	275	313	3000 / H <sub>2</sub> SO <sub>4</sub>	<b>10</b>
THULIUM	360	455	7 / K <sub>2</sub> CO <sub>3</sub>	<b>750</b>

Table 1 : Main  $\lambda_{\text{excitation}}$ ,  $\lambda_{\text{fluorescence}}$ , lifetimes and limits of detection in TRLIF

### 4. RESULTS

*In the environment*, determination of uranium and curium at ultra low level are required for cartography purposes. Figure 3 represents the fluorescence spectrum of uranium at 0.5 ng/l in phosphoric acid. This value, roughly corresponds to 10<sup>7</sup> molecules in the interaction volume.

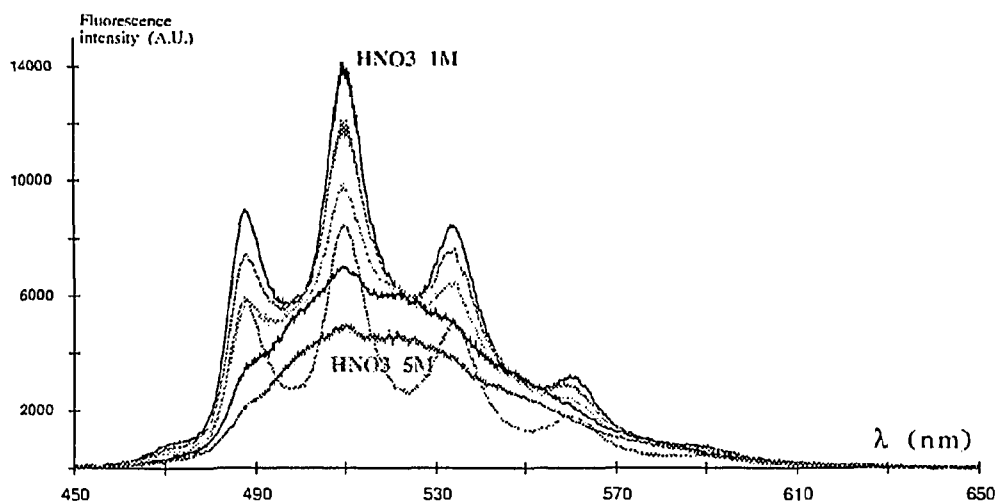


Figure 5 : Uranium fluorescence spectra as a function of nitric acid concentration

*In waste storage assessment*, the knowledge of radioelement behaviour is of great importance. In particular, complexation reactions of radioelements with natural organic ligands such as humic substances (humic/fulvic acids) present in aquifer systems are important, because of the strength of complexes that humic substances form with cations, in particular trivalent elements like americium and curium. TRLIF is the only technique that allow to work *directly* at trace levels. The complexation of curium by humic substances leads to an increase of the curium fluorescence signal until saturation of the complexing sites occurs. From titration curves (figure 6), binding parameters such as the complexing capacity  $W$  and the conditional stability constant  $\beta$  (by non linear regression fit) are obtained. TRLIF as shown the influence of cation concentration on the interaction constant  $\beta$  as well as the independence of  $\beta$  with pH.

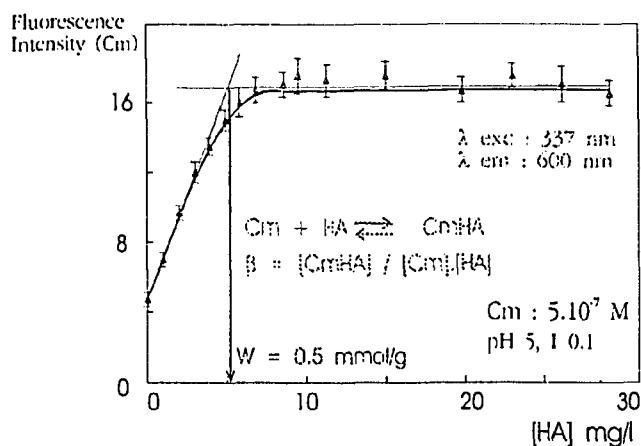


Figure 6 : Typical fluorescence titration curve of Cm with HA by TRLIF

As for speciation of uranium in the Purex process (directly in nitric acid), TRLIF is used for speciation of uranium in condition representative of future waste disposal sites as shown on

figure 7 where the fluorescence spectrum at pH 2 is only due to  $\text{UO}_2^{2+}$  (with the four characteristic peaks but is drastically modified at pH 5 due to the presence of both  $\text{UO}_2^{2+}$  and  $\text{UO}_2(\text{OH})^+$ . By spectral deconvolution, it is possible to determine the amount of each species present in solution and by doing so to perform speciation. Moreover, lifetimes of these different species are very different and allow in certain cases time resolution.

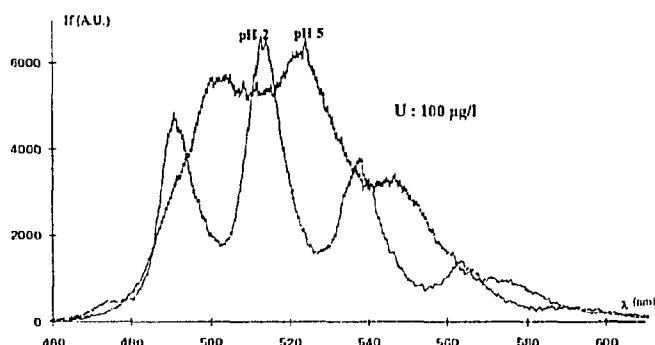


Figure 7 : Fluorescence spectra (normalized) of uranium at pH 2 and 5. I 0.1M

## 5. CONCLUSION

Time-Resolved Laser- Induced Fluorescence is a fast, sensitive and selective technique for fluorescent actinides and lanthanides determinations in the nuclear fuel cycle. These features have allowed to use TRLIF in various fields from ultratrace analysis to complexation studies (fluorescence titration, spectral deconvolution). Furthermore, the use of fiber optics and optodes allows remote measurements in hostile or difficult to access environment and is promising for in-line analysis in the reprocessing or for environmental monitoring.

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<sup>4</sup> For simplification purposes, only references from the CEA are quoted in this paper