



HAL
open science

Design and development of a microfluidic system for quantification by UV-visible spectroscopy in hostile environments

Elodie Mattio, Audrey Soler, Isaac Rodríguez-Ruiz, Sophie Charton, M. Miguirditchian, Fabrice Lamadie

► To cite this version:

Elodie Mattio, Audrey Soler, Isaac Rodríguez-Ruiz, Sophie Charton, M. Miguirditchian, et al.. Design and development of a microfluidic system for quantification by UV-visible spectroscopy in hostile environments. 22nd ICFIA - International conference on flow injection analysis and related techniques, May 2020, Marseille, France. . hal-04722614

HAL Id: hal-04722614

<https://hal.science/hal-04722614v1>

Submitted on 5 Oct 2024

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

DESIGN AND DEVELOPMENT OF A MICROFLUIDIC SYSTEM FOR QUANTIFICATION BY UV-VISIBLE SPECTROSCOPY IN HOSTILE ENVIRONMENTS

Elodie Mattio¹, Audrey Caleyron¹, Isaac Rodriguez-Ruiz²,
Sophie Charton¹, Manuel Miguiditchian¹, Fabrice Lamadie¹

¹CEA, DES, ISEC, DMRC, University of Montpellier, Marcoule, France

²Laboratoire de Génie Chimique - CNRS, UMR 5503, Toulouse, France

CONTEXT

The development and study of new recycling processes for **spent nuclear fuel** rely on **analysis** and **instrumentation** at all stages. Due to this, over the last few years **analysis devices adapted to the monitoring of different processes** (dissolution, liquid/liquid extraction, precipitation, etc.) have been increasingly designed and developed. For scientific reasons (small-scale studies, thermodynamic studies, etc.) but also **to minimize costs, risks and waste**, these developments are increasingly carried out on **milli/microfluidic devices**. In this work we prove that **photonic lab-on-a-chip** (PhLoC) technology is **fully suitable for monitoring all actinides concentration** along the plutonium uranium refining extraction (PUREX) process. For this purpose, the **evaluation of a complete optofluidic analytical approach**, suitable for operation in a confined enclosure, such as a glove box, is carried out for the analysis of **uranium (IV), uranium (VI), and plutonium (IV)** pure solutions and mixtures, with the aim of subsequently developing complete microfluidic analytical systems resulting in the detection of actinides using spectrophotometric techniques.

URANIUM - FUME HOOD

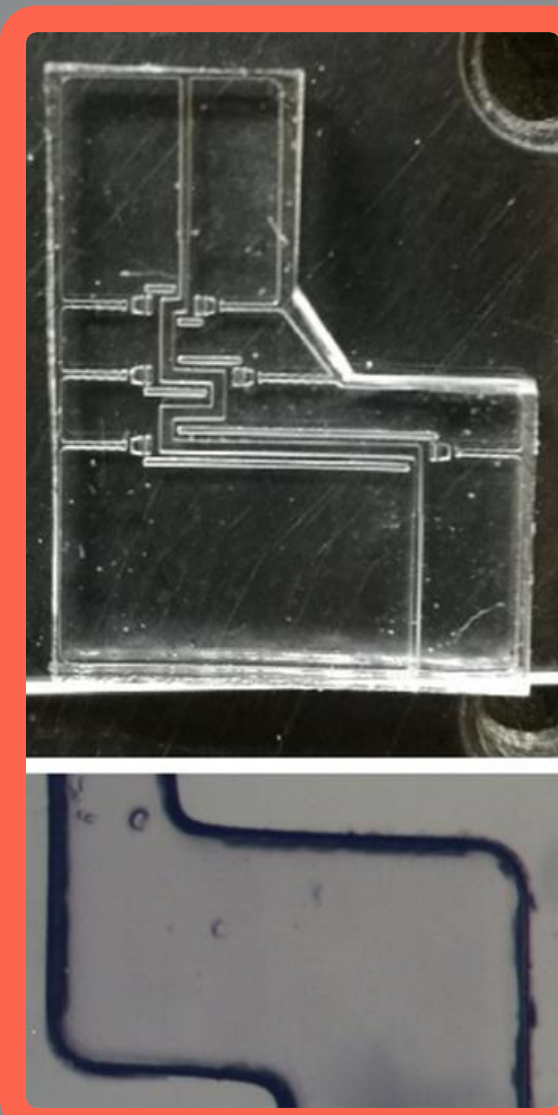
CHIP DESIGN

For **uranium experiments**, a **PDMS chip** was used. The PhLoC design consists of a **single microfluidic serpentine channel**, with a total volume of **~3-5 μL** , interrogated in **3 optical paths** of 1, 2.5, and 10 mm.

The optical paths are ended by **2D collimation microlenses**. **Two air mirrors** are placed along each side of the microfluidic channel to **avoid light cross-contamination** among channels. Self-aligning channels allow the hassle free positioning of pigtailed 240 μm fiber optics into the micro optical setup.

For sample injection, **two stainless steel needles** were side-coupled and glued to the microfluidic channel, in order to provide a **nearly zero-volume interface connection** with any sample injector.

Finally, the chip was placed in a **protective housing** equipped with a lockable viewing hatch, which physically protects the chip and isolates it from the surrounding light sources.

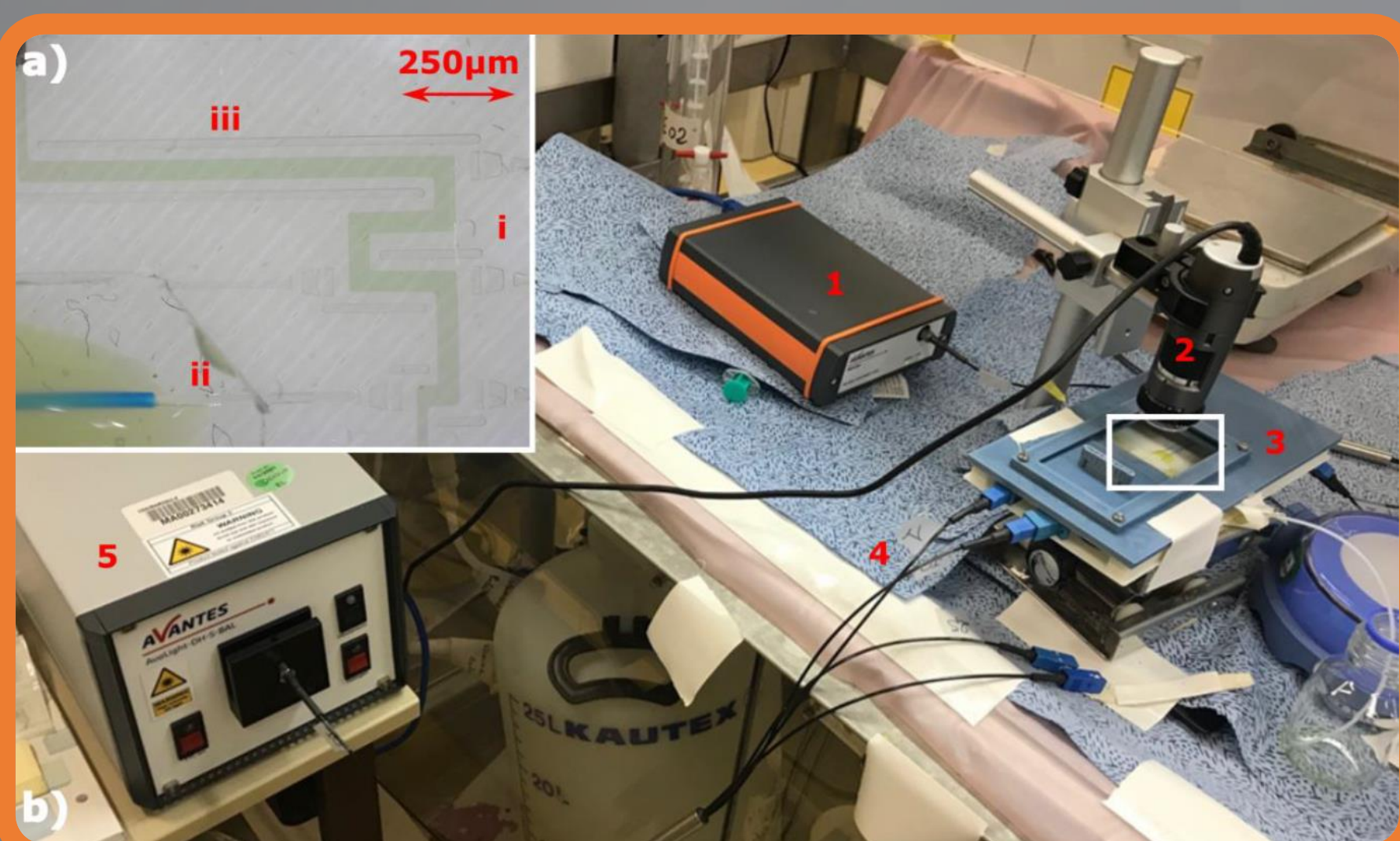


PDMS chip and microscopic view of the 1 mm optical path

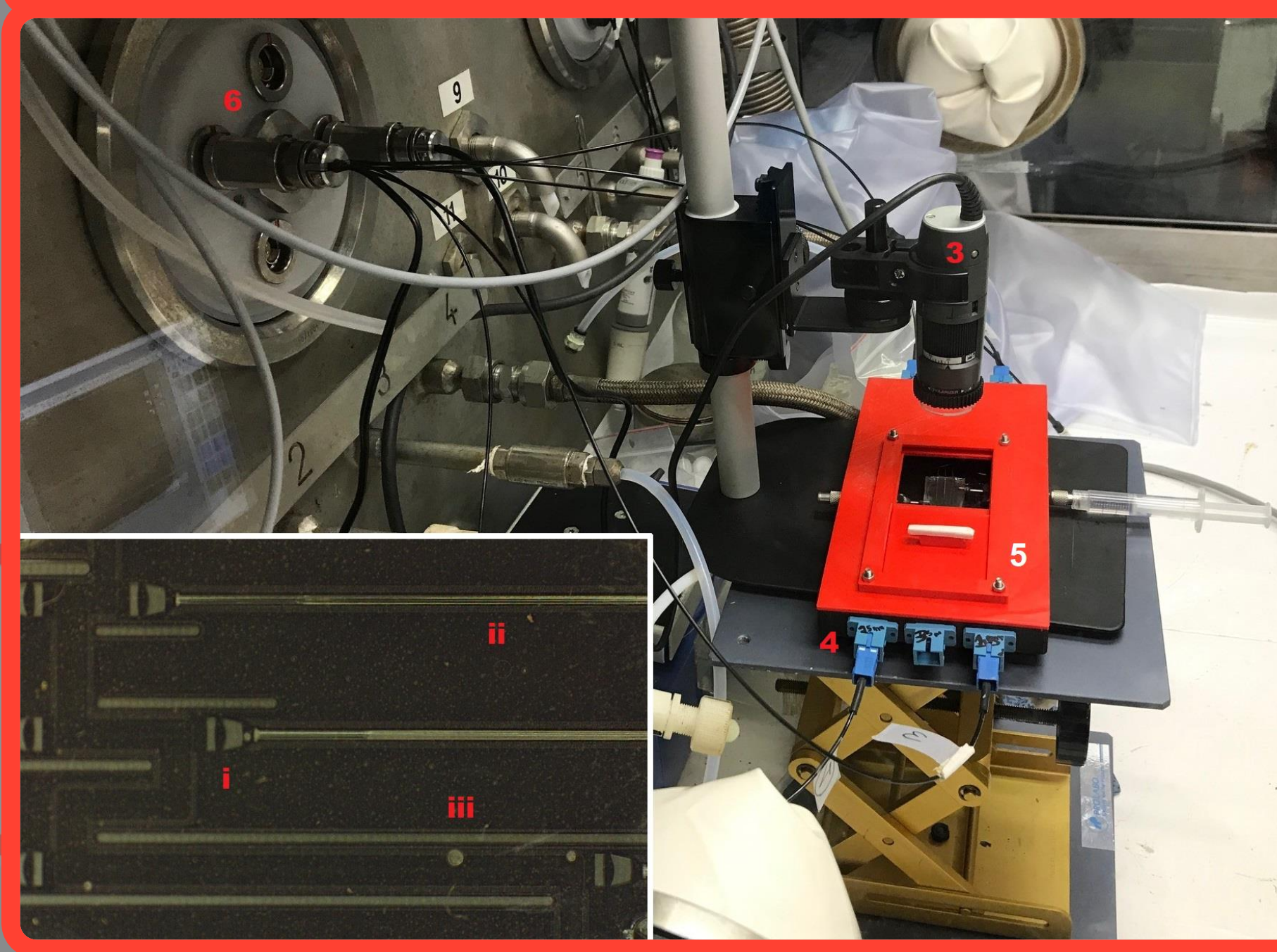
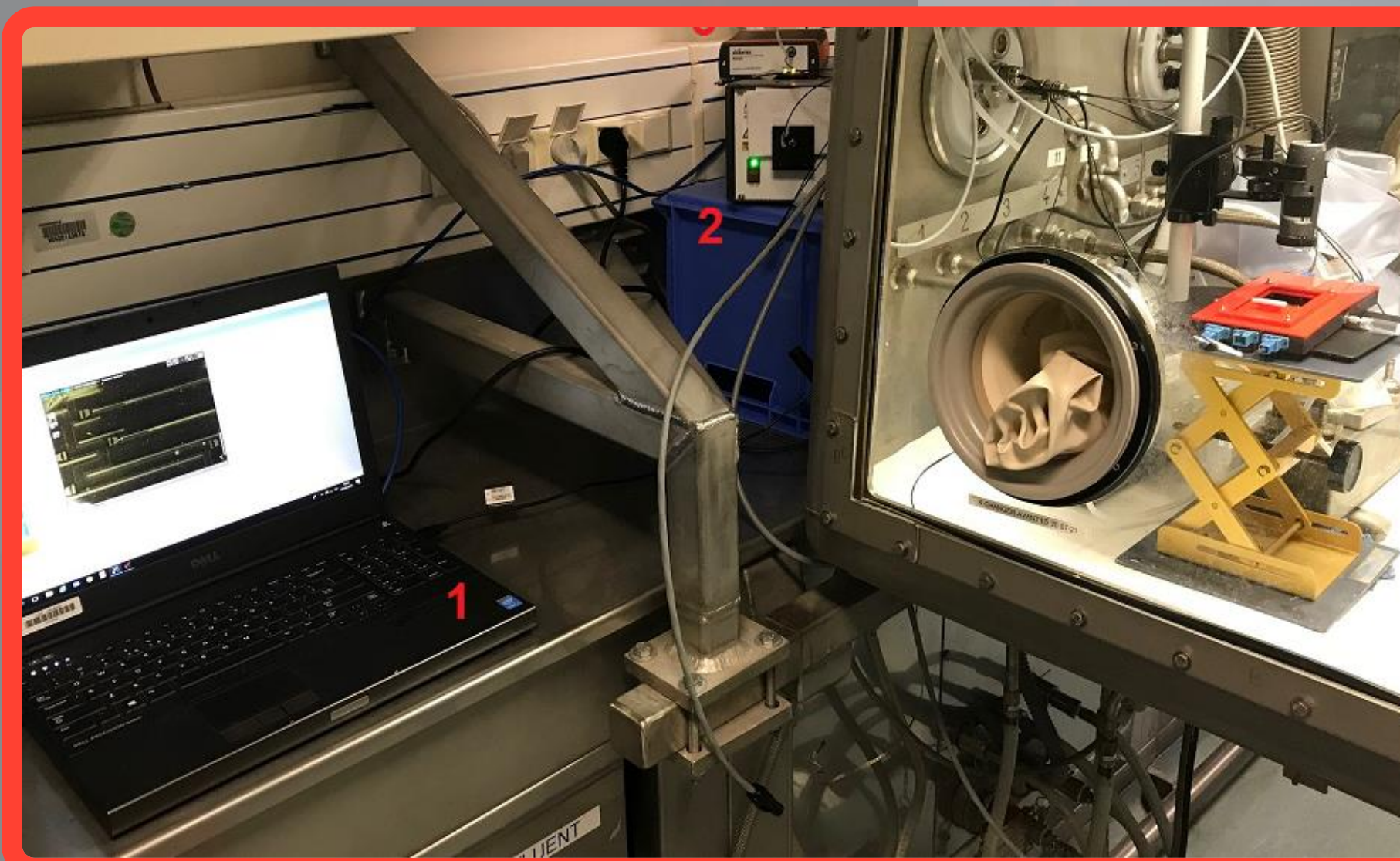
SETTING UP IN A LABORATORY FUME HOOD

a - Zoom on the chip using a portable microscope, the mirrors (iii), lenses (i) and self-aligning channels (ii) of the fibers are visible.

b - Photography of the full setup :
1 - Spectrometer ;
2 - Portable microscope ;
3 - PhLoc inside its protection holder ;
4 - Fibers Optics ;
5 - Deuterium-halogen light.



PLUTONIUM



Zoom on the glass chip for plutonium, using microscopic camera : microlenses (i), self-aligning channels (ii), and mirrors (iii).

GLOVE BOX

For the **plutonium analyses**, a **glass chip** (with an analogous design to the PDMS), ensuring tighter and **more robust fluidic connections**, was mounted in a 3D-printed housing holding both fluidic and optical connections, and **inserted into the glove box**.

This chip was manufactured by FEMTOprint (Switzerland).

SETTING UP IN A GLOVE BOX

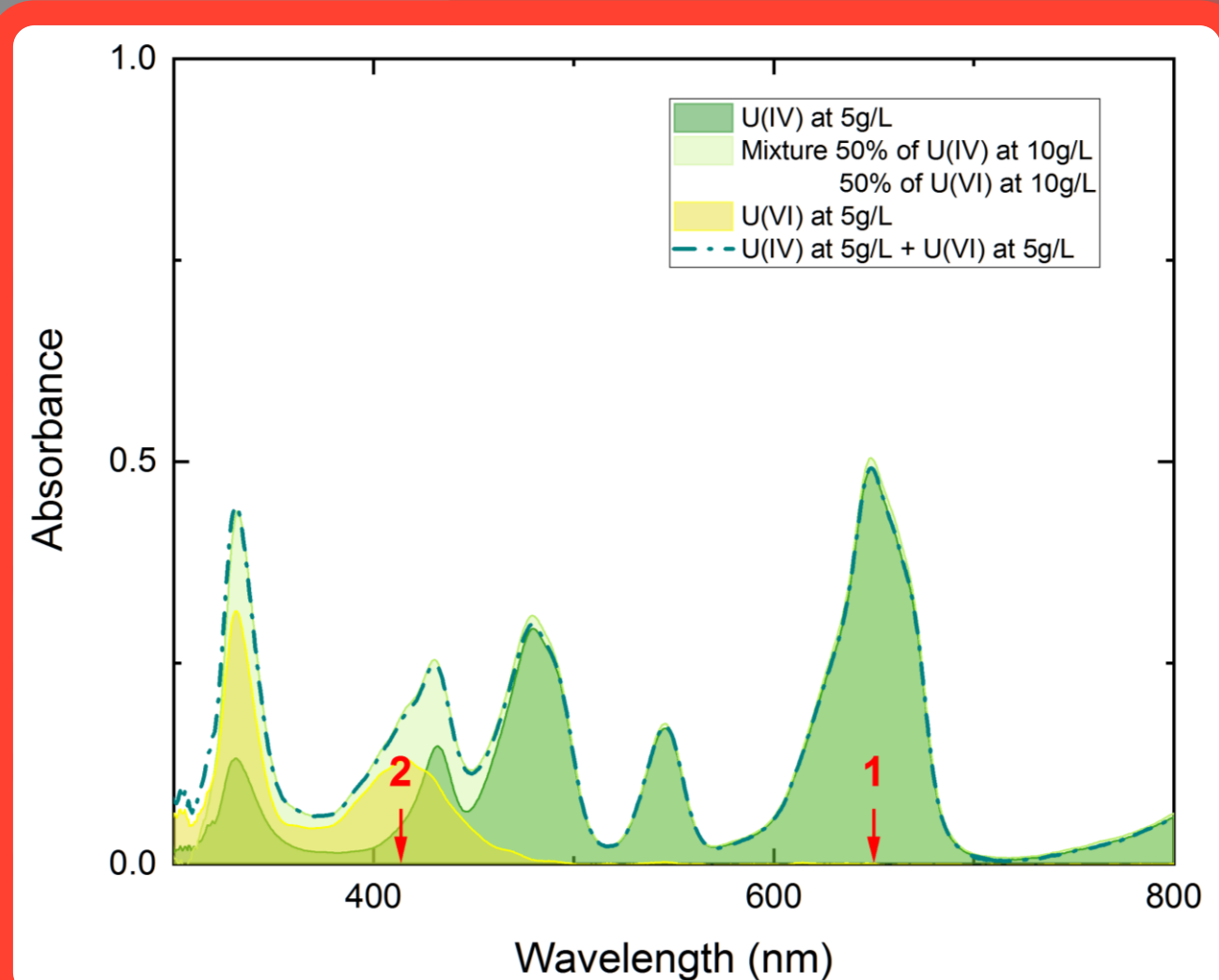
The light source, the **computer** and the **spectrophotometer** are located **outside the glove box**. The chip is connected to them using **fiber optics mounted on an instrumented hole-plug**, which also connects the **USB microscopic camera** to the computer.

Setup implementation :

- 1 - Laptop ;
- 2 - Source + spectrometer ;
- 3 - Portable microscope ;
- 4 - Fibers optics ;
- 5 - PhLoc inside its protection holder ;
- 6 - Instrumented hole-plug.

QUANTIFICATION OF A MIXTURE OF URANIUM AT TWO OXIDATION STATES

To determine the proportion and the concentration of each oxidation state of uranium in a given mixture, we considered that the absorbance is a **linear combination** of the absorbance of the pure solutions weighted by their respective proportions.



Spectra of a 50/50 mixture of U(VI) and U(IV) and pure corresponding solutions.

Absorbance is measured at **two wavelengths**, in order to build a system of two equations with two unknowns, that allows the determination of the concentration of each oxidation state :

$$A_M(\lambda_1) = (\alpha \times \epsilon_{U(VI)}(\lambda_1) \times C_{U(VI)} + (1 - \alpha) \times \epsilon_{U(IV)}(\lambda_1) \times C_{U(IV)}) \times L$$

$$A_M(\lambda_2) = (\alpha \times \epsilon_{U(VI)}(\lambda_2) \times C_{U(VI)} + (1 - \alpha) \times \epsilon_{U(IV)}(\lambda_2) \times C_{U(IV)}) \times L$$

$A(\lambda) \rightarrow$ Mixture absorbance at the considered wavelength ;

$L \rightarrow$ length of the optical path ;

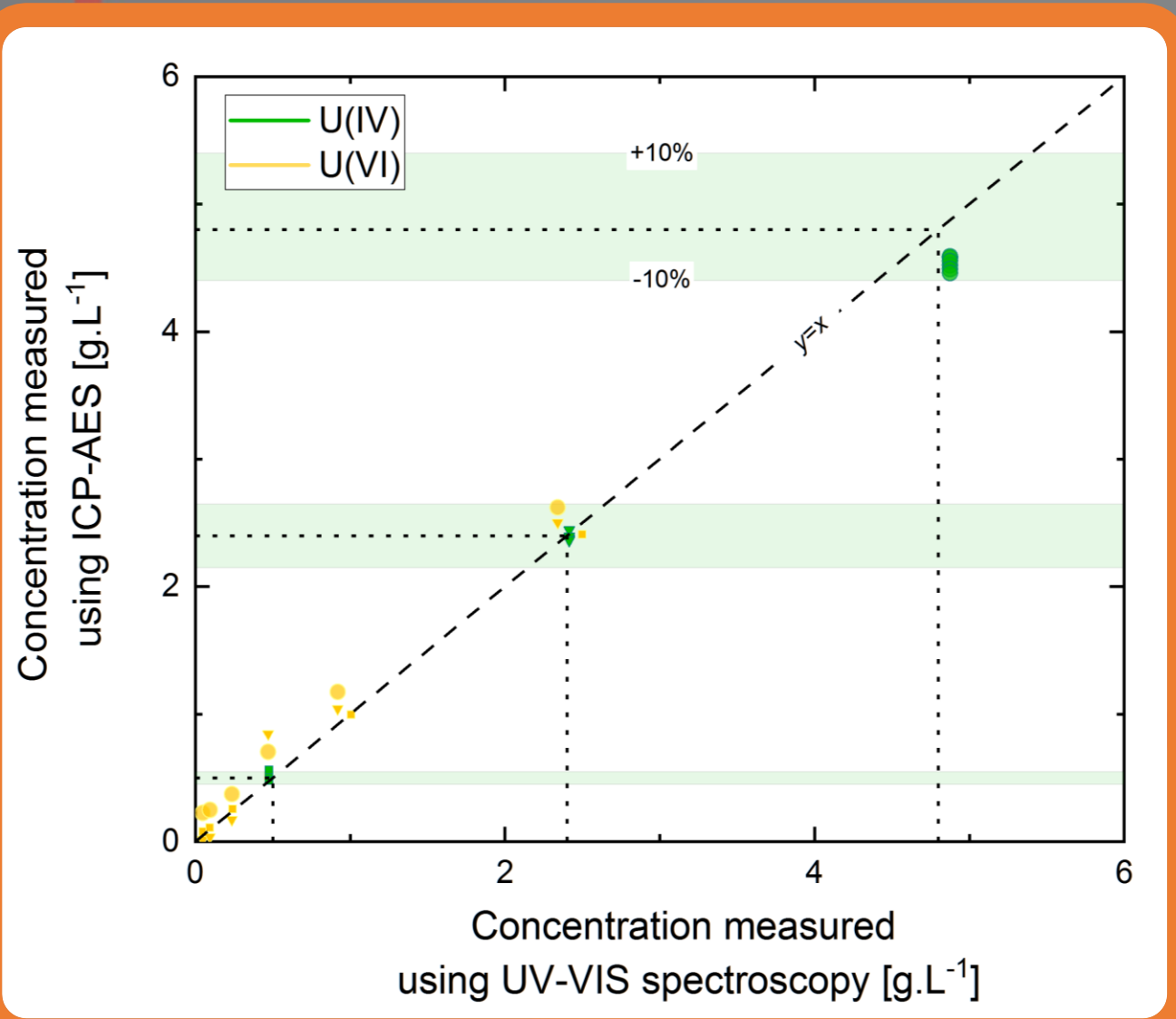
$\epsilon \rightarrow$ molar attenuation coefficient ;

$\lambda_1 = 649.9 \text{ nm}$ and $\lambda_2 = 413.6 \text{ nm}$;

$\alpha \rightarrow$ U(IV) proportion in the mixture

Comparison with ICP-AES measurements

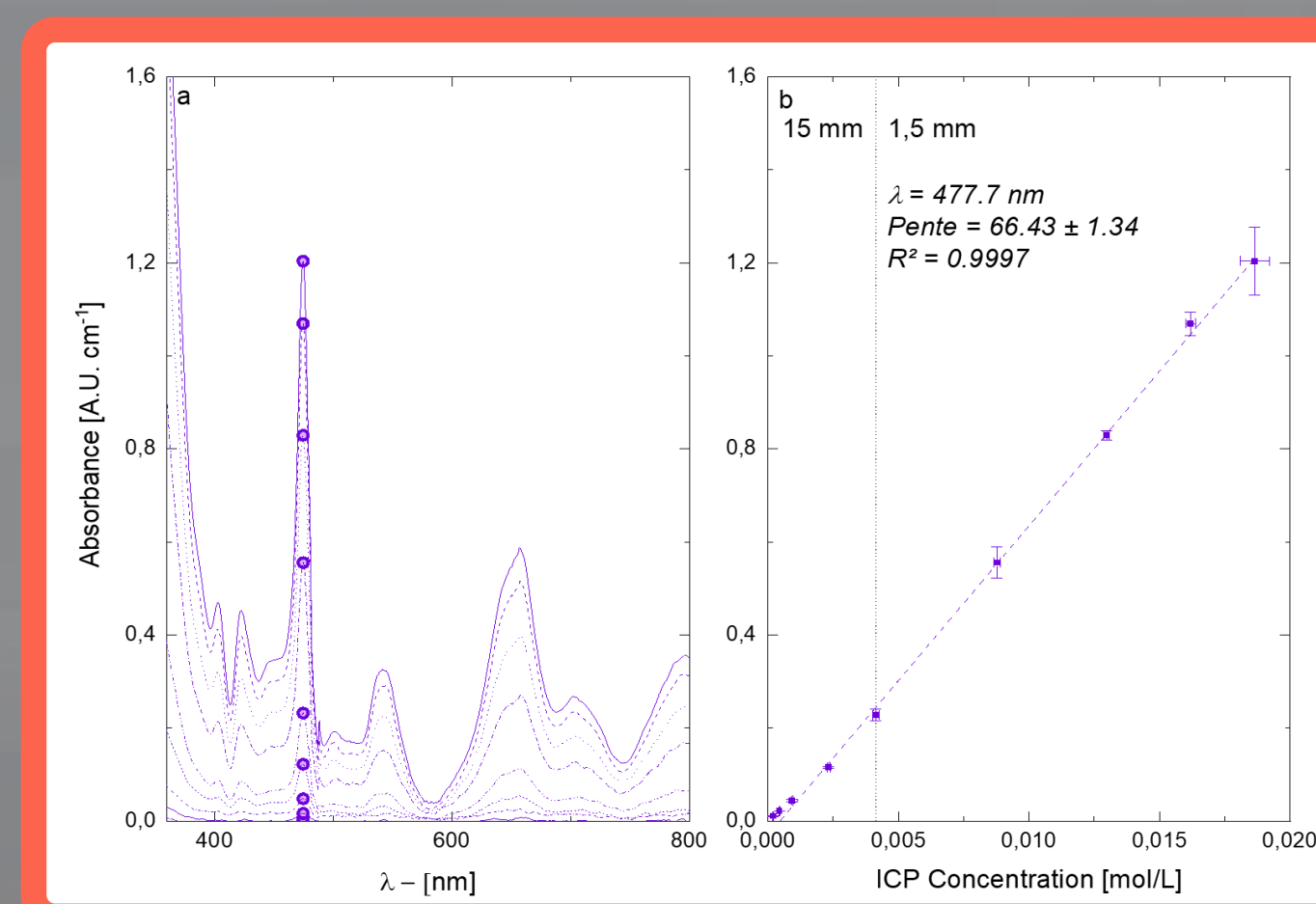
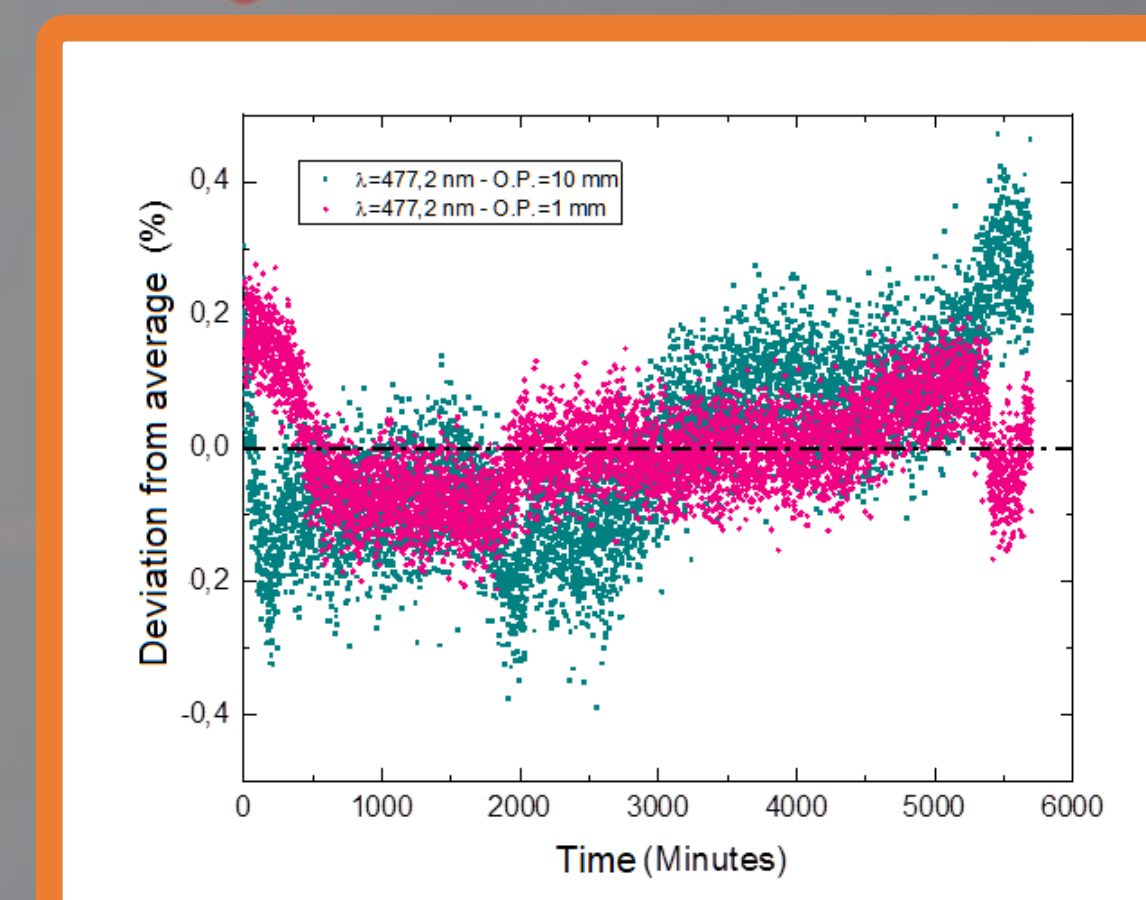
on the same solutions confirms the relevance of PhLocs analysis, with in all cases less than 10% difference between the two techniques.



Comparison of the concentrations obtained by the implemented method with those obtained by ICP-AES

LIGHT STABILITY

To evaluate the influence of **glove box depressurization** on light stability, a study was performed on two optical paths by recording a spectrum every minute for 4 days. The results show that the environmental factors cause a variation of **less than 0.5%**.



Spectra of plutonium (IV) solutions between 350 and 800 nm, and corresponding calibration curve.

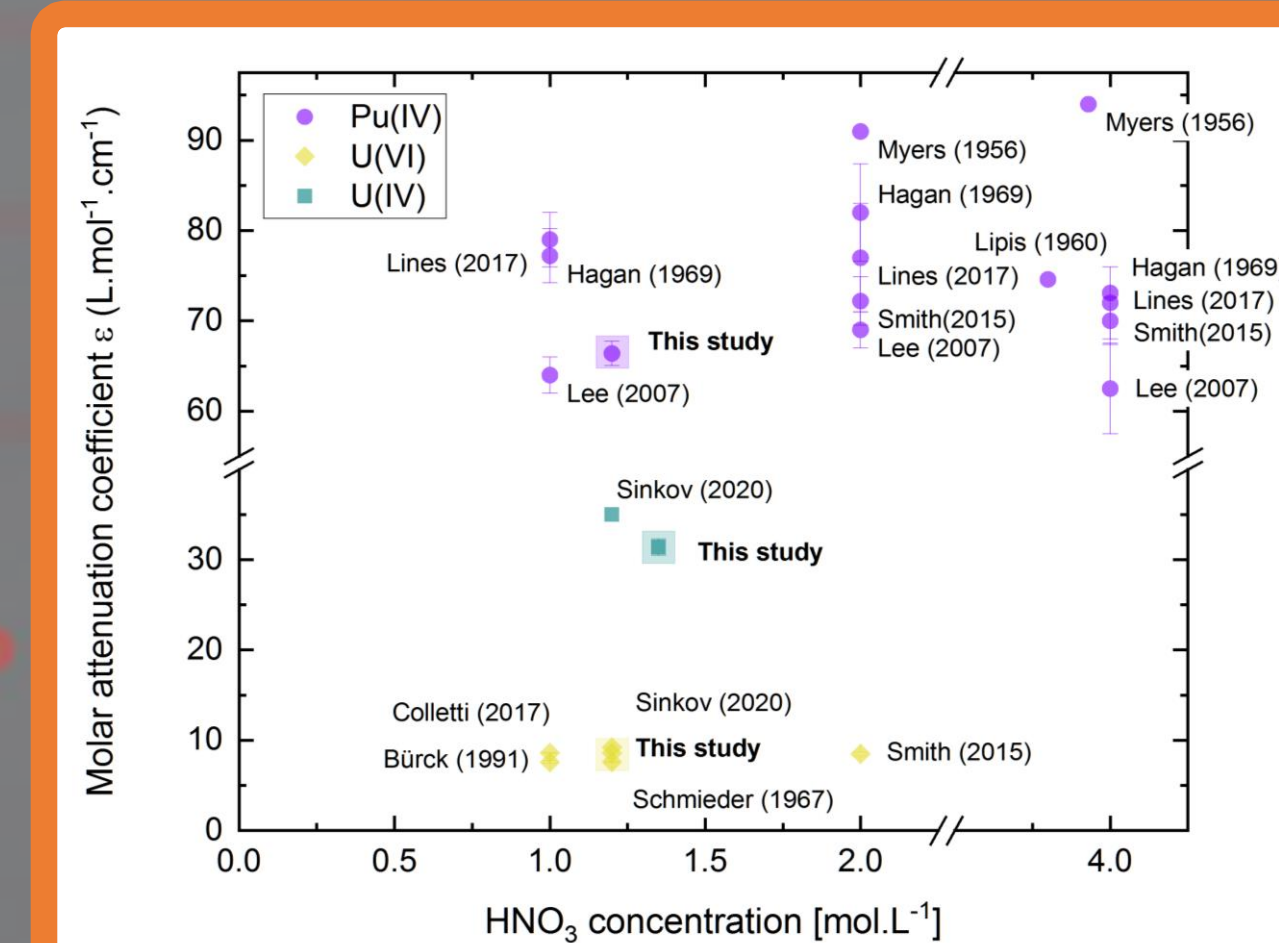
PLUTONIUM QUANTIFICATION

Several solutions of Pu(IV) have been analyzed on the 1.5 and 15 mm optical paths. A **linear relationship** has been established between absorbance at $\lambda = 477.7 \text{ nm}$ and concentration.

A limit of detection **10.2 $\mu\text{mol.L}^{-1}$** was obtained for Pu(IV).

MOLAR ATTENUATION COEFFICIENTS

The quality of these results is confirmed by **comparing the molar attenuation coefficients** with literature data, showing complete agreement with previous results obtained with milliliter solutions.



Graphic comparison between the results obtained on optofluidic devices and the state of the art from the literature.

CONCLUSION AND PERSPECTIVES

The results presented here validate the use of a **photonic lab-on-chip** approach for in-field **analysis of actinide solutions**. The PhLoCs used here allow the measurement of several types of actinides (plutonium, uranium, etc.) in different oxidation states, in confined nuclear environments such as **sealed containers** (glove boxes or fume hoods), over **wide concentration ranges** and, above all, with the same degree of **simplicity and accuracy** as a lab-scale UV-Vis spectrometer, but using minute amounts of sample (between 10 and 140 μL depending on the chip) to cover a range of analyzable concentrations of **three orders of magnitude**. Moreover, the proposed coupled spectroscopic approach is fully **applicable to the characterization of other chemical species**, such as lanthanides or transition metals, opening huge perspectives for on-line process monitoring.