



**HAL**  
open science

## Anion exchange microsystems for radionuclides separation in nitric acid media

M. Losno, R. Brennetot, C. Mariet, I. Ferrante, S. Descroix

### ► To cite this version:

M. Losno, R. Brennetot, C. Mariet, I. Ferrante, S. Descroix. Anion exchange microsystems for radionuclides separation in nitric acid media. RANC 2016 - 1st international conference in radioanalytical and nuclear chemistry, Apr 2016, Budapest, Hungary. cea-02509773

**HAL Id: cea-02509773**

**<https://cea.hal.science/cea-02509773>**

Submitted on 17 Mar 2020

**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.



DE LA RECHERCHE À L'INDUSTRIE

cea den



**Marion Losno, René Brennetot,  
Clarisse Mariet <sup>1</sup>**

<sup>1</sup> Den – Service d'Etudes Analytiques et de  
Réactivité des Surfaces (SEARS), CEA,  
Université Paris-Saclay, F-91191, Gif sur Yvette,  
France

**Ivan Ferrante, Stéphanie Descroix <sup>2</sup>**

<sup>2</sup> MMBM Group, Institut Curie Research Center,  
CNRS UMR 168, Paris, France

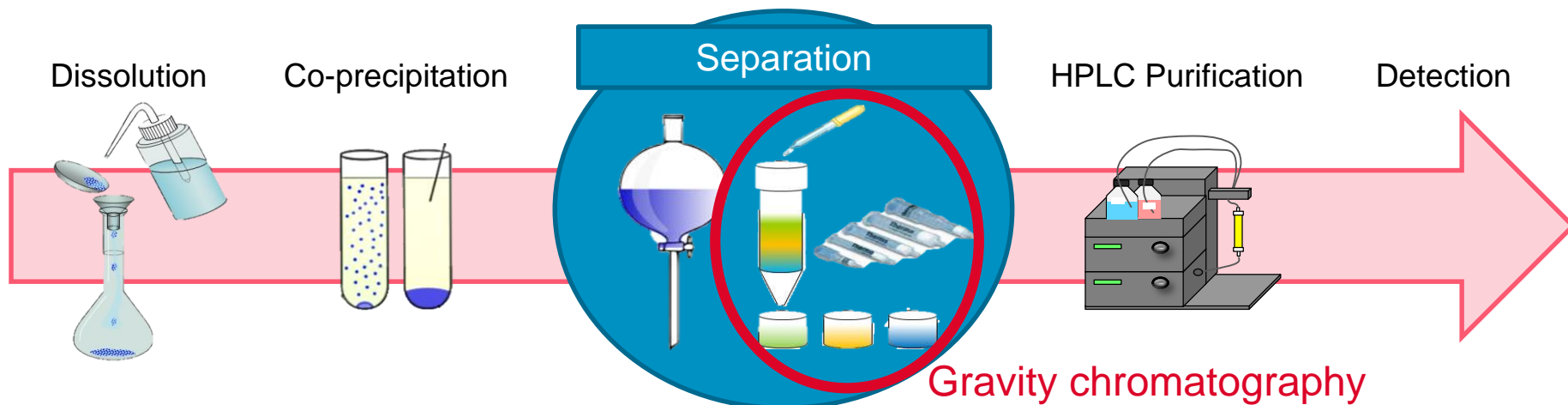
# ANION EXCHANGE MICROSYSTEMS FOR RADIONUCLIDES SEPARATION IN NITRIC ACID MEDIA

RANC 2016 | Marion Losno

April 12th, 2016

**RANC**  
April 10-15, 2016  
Budapest, Hungary

1st International  
Conference on  
Radioanalytical and  
Nuclear Chemistry



- Many constraints have to be taken into account such as
  - Glove box handling
  - Concentrated irradiant samples
  - Waste management

## ☺ Benefits of miniaturization

- A little amount of sample needed for the analysis
  - Decrease of the volume handled by the operators
  - Decrease of the dose received
  - Decrease of the amount of waste produced -> reduces analysis cost



## ■ Benefits related to plastic devices

- Easy to produce (thermoformable)
- Disposable : no cross-contamination

## ■ Benefits related to lab-on-CDs

- No need for external pumping device or connection
- Very limited instrumentation (only a rotor) -> limited cost of maintenance
- Easy automation and multiplexed analysis

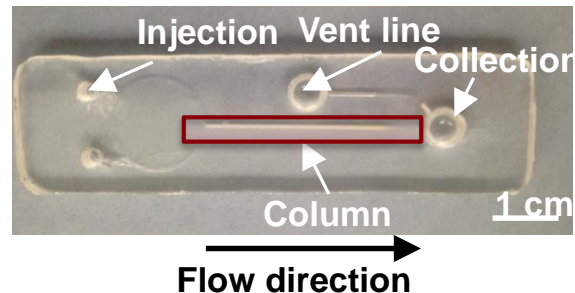


 How to develop this type of technology ?

- Step 1 : Lab-on-CD configuration \*
  - CD platform made of PEEK including 4 microsystems holders



- Step 2 : microsystem design \*
  - Use of Cyclo Olefin Copolymer (cheap, easy to structure and suited physico-chemical properties)



- Step 3 : implementation of a monolithic anion-exchange stationary phase for radionuclides separation

## ■ Constraints due to the analysis

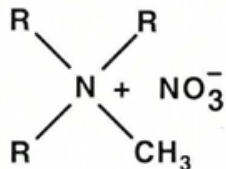
### ■ Nitric acid resistance

- Corresponding to the dissolution medium of radiochemical samples

When  $[\text{HNO}_3] > 4\text{mol.L}^{-1}$  \*

- Formation of  $[\text{UO}_2(\text{NO}_3)_x]^{(2-x)}$  ( $1 \leq x \leq 3$ ) **anionic complex**
- **Cationic form** of lanthanides ( $\text{Ln}^{3+}$ )

- Functionalization by an anion exchanger will enable the separation of the two components in  $[\text{HNO}_3] > 4 \text{ mol.L}^{-1}$



Quaternary ammonium was chosen for its efficiency at macro scale

\* Chiarizia, R., R. Gatrone and E. Horwitz (1995). "Am (III) and Eu (III) extraction by Aliquat-336 and benzyl substituted quaternary ammonium salts from nitrate and thiocyanate solutions." Solvent Extraction and Ion Exchange **13**(4): 615-645.

- Stationnary phase constraints
    - Easy to synthesize
    - Localization of the phase
- } ☺ Photochemistry

Stationnary phase = polymer + grafting of a molecule of interest

- Choice of organic methacrylate monolith [1]

- Photosynthesizable
- Localized
- Chemical resistance
- Mechanical resistance
- Low flow resistance

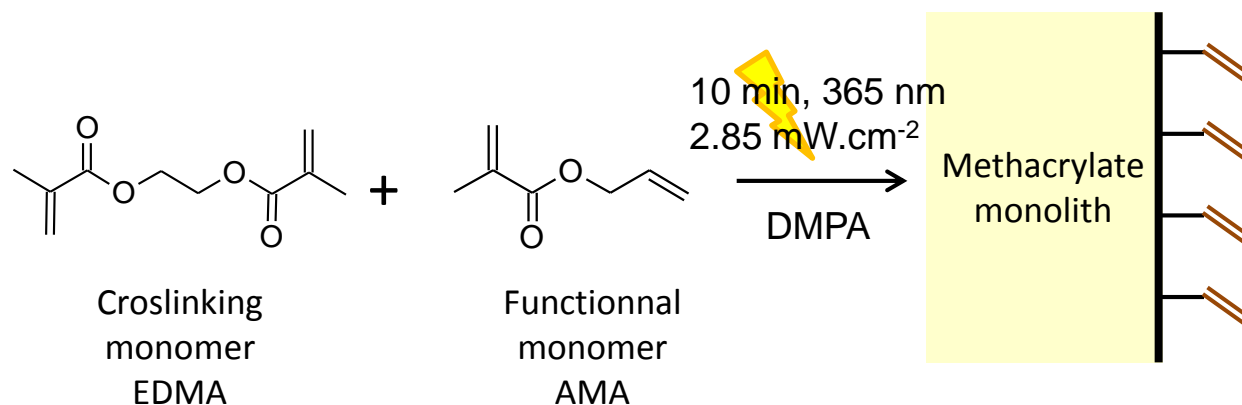
- Choice of thiolene « click chemistry » [2]

- Photochemical reaction
- Localized
- Chemical resistance
- Versatility

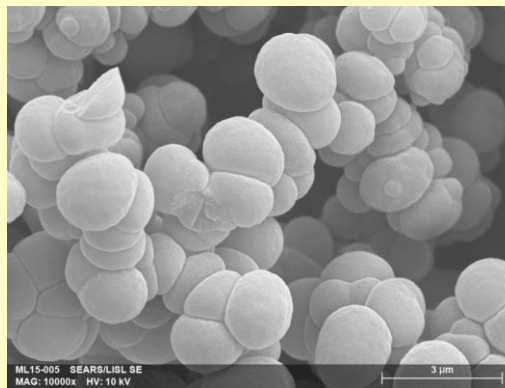
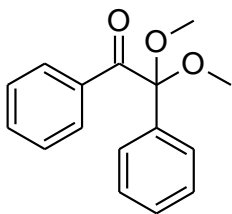
[1] Svec, F. and J. M. J. Fréchet (1996). "New designs of macroporous polymers and supports: From separation to biocatalysis." *Science* **273**(5272): 205-211.

[2] Kolb, H. C., M. G. Finn and K. B. Sharpless (2001). "Click chemistry: Diverse chemical function from a few good reactions." *Angewandte Chemie International Edition* **40**(11): 2004-2021.





- Monomers : 24 wt% Ethylene glycol dimethacrylate (EDMA) and 16 wt% Allylmethacrylate (AMA)
- Porogenic solvent : 24 wt% 1,4-butanediol, 35 wt% 1-propanol, 1 wt% water
- Photoinitiator : 1 wt% DMPA



Globule size  $\approx 1 \mu\text{m}$

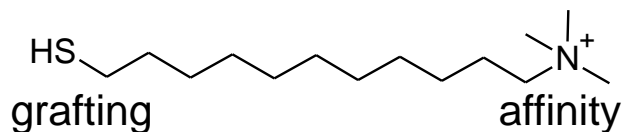
Permeability  $\approx 10^{-14} \text{ m}^2$

Density  $\approx 0.4 \text{ g.mL}^{-1}$

Total porosity  $\approx 60 \%$

## Choice of molecules

- Molecule to be grafted

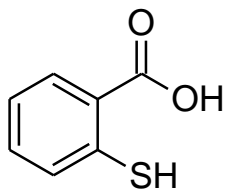


→ Study of the reaction through different molecules

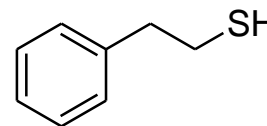
### Ammonium thiol

- ☺ Commercially available
- ☹ Price
- ☹ Characterization

### Thiosalicylic acid

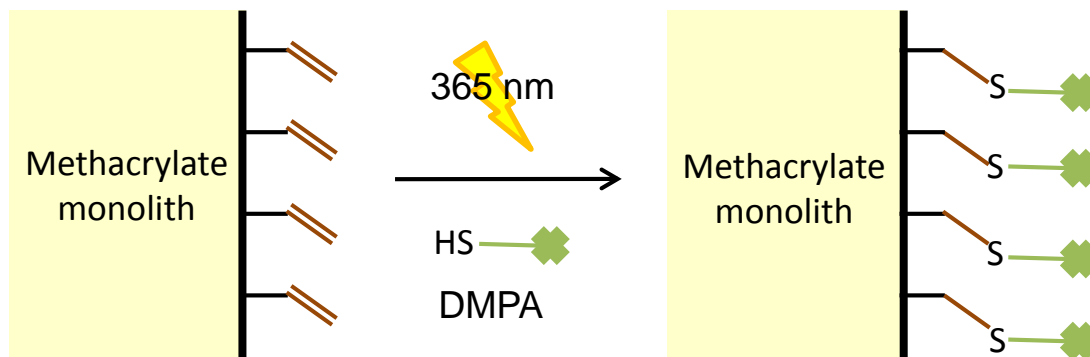


- ☺ Commercially available
- ☺ Price
- ☺ Characterization

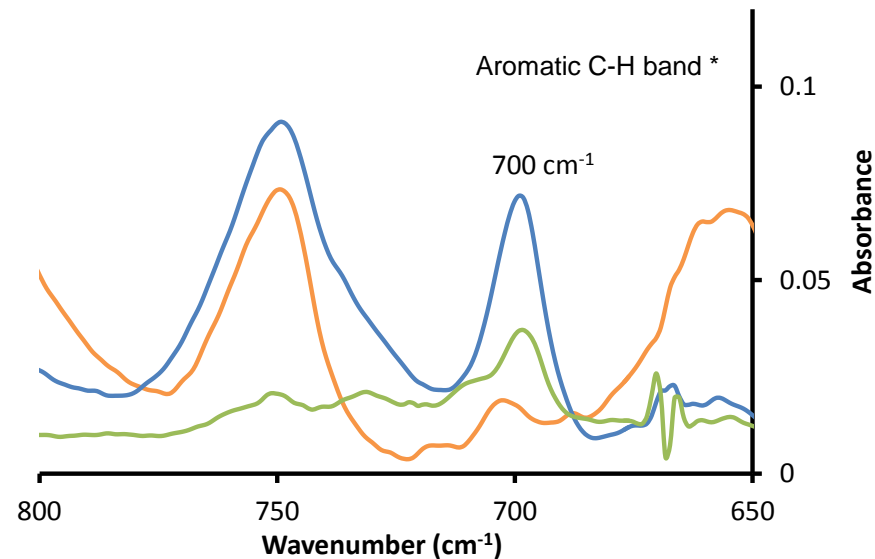
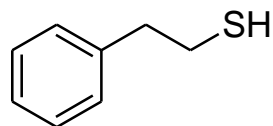
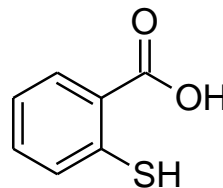
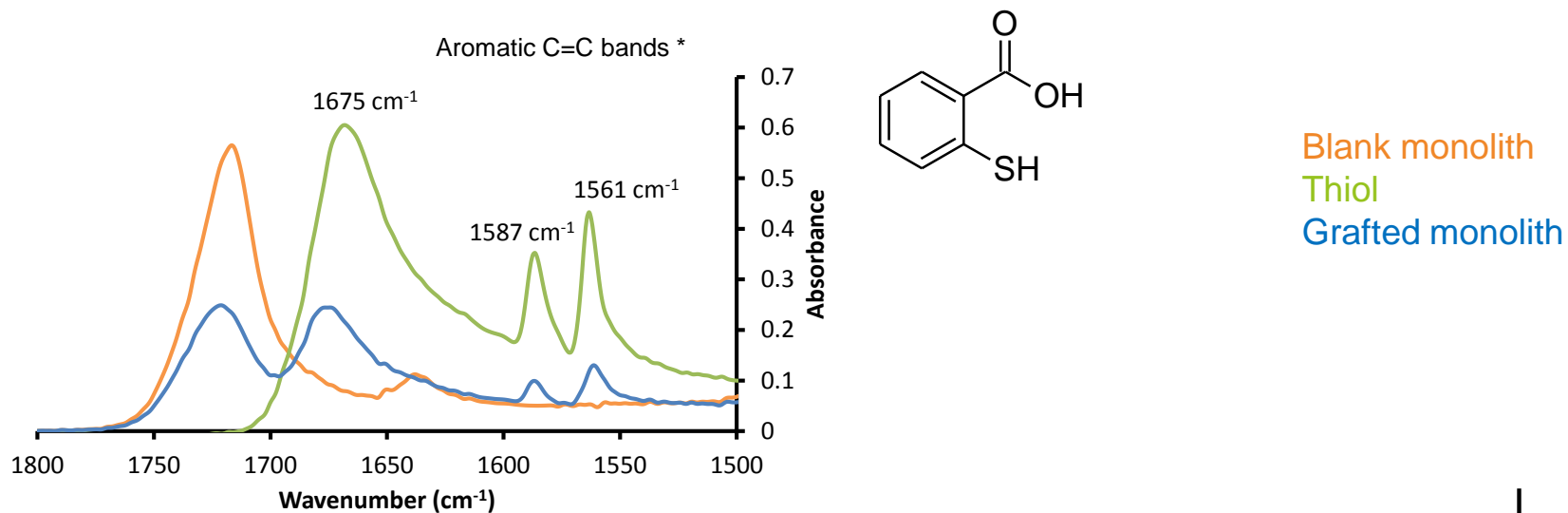


2-phenylethanethiol

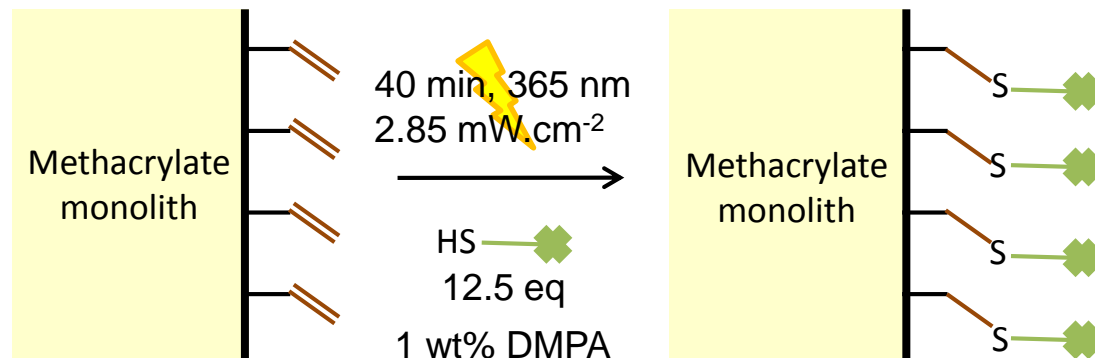
## Procedure



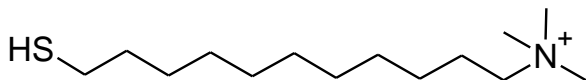
## VERSATILITY OF FUNCTIONALIZATION

\* Skoog, D. A., D. M. West and F. J. Holler (1997). *Chimie analytique*. Bruxelles, Boeck and Larcier.\* Silverstein, Basler and Morill (1998). *Identification spectrométrique de composés organiques*, Boeck and Larcier.

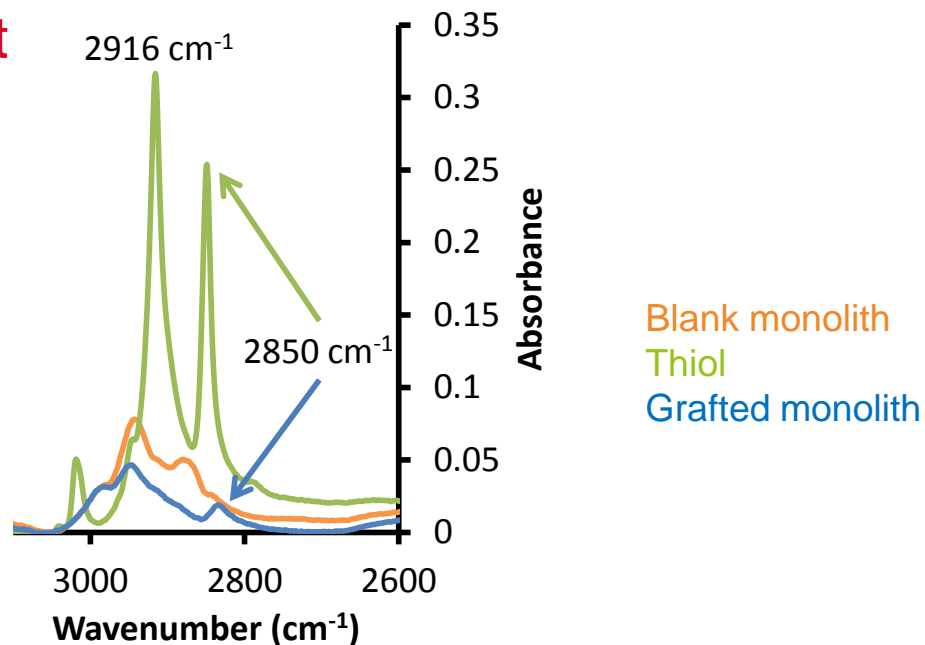
## Optimized conditions



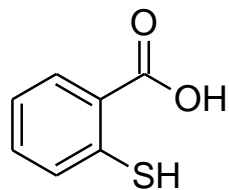
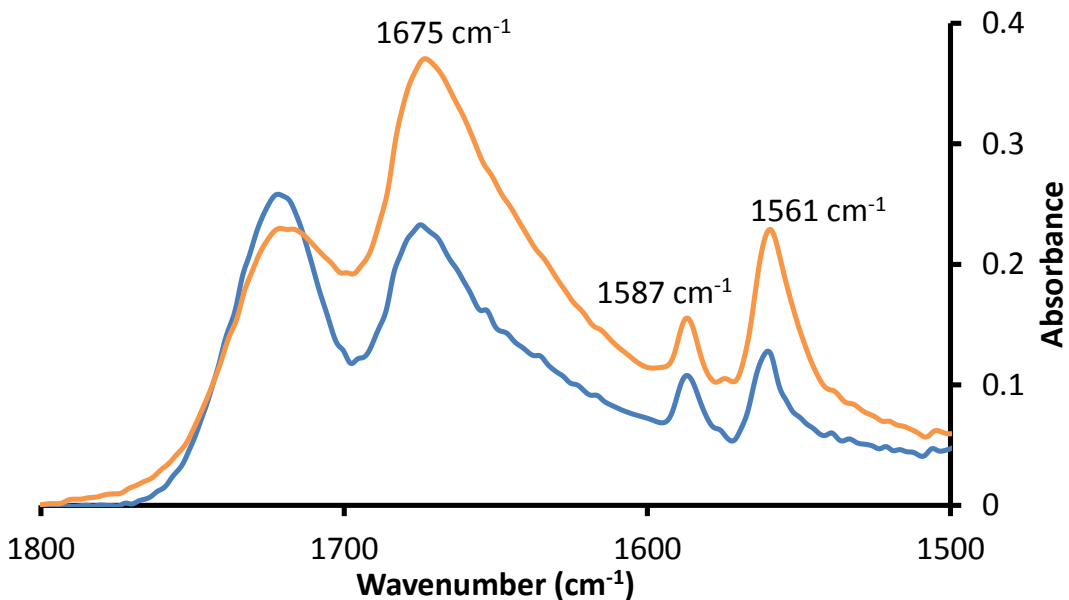
## Molecule of interest



Versatile functionalization

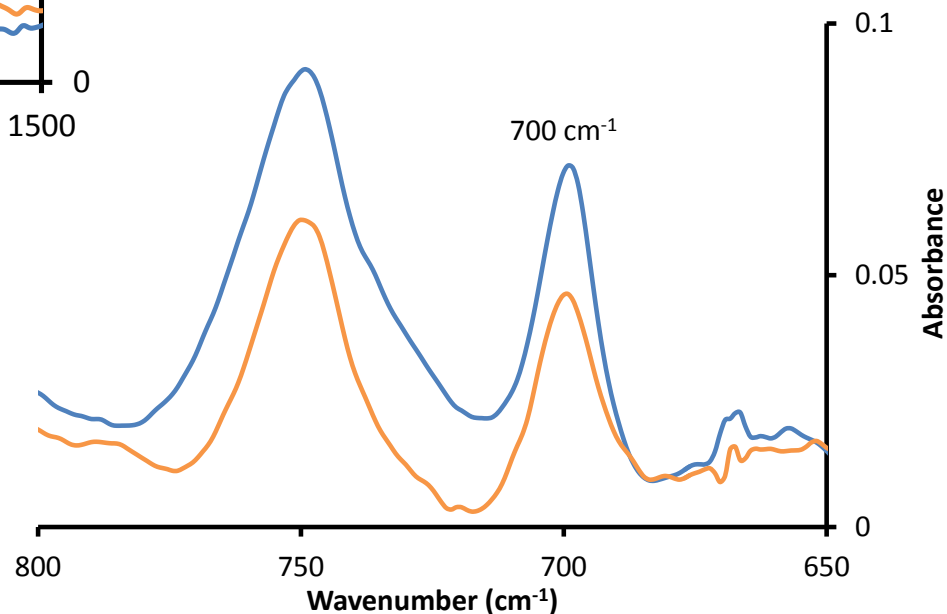
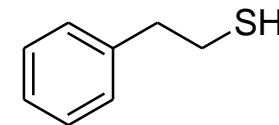


# CHEMICAL RESISTANCE OF THE FORMED C-S BOND



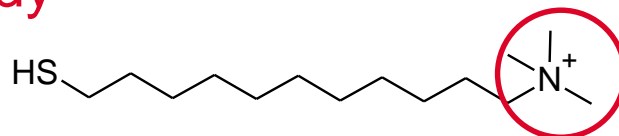
Grafted monolith

Grafted monolith after 24 h in a 8 mol.L<sup>-1</sup> nitric acid aqueous solution

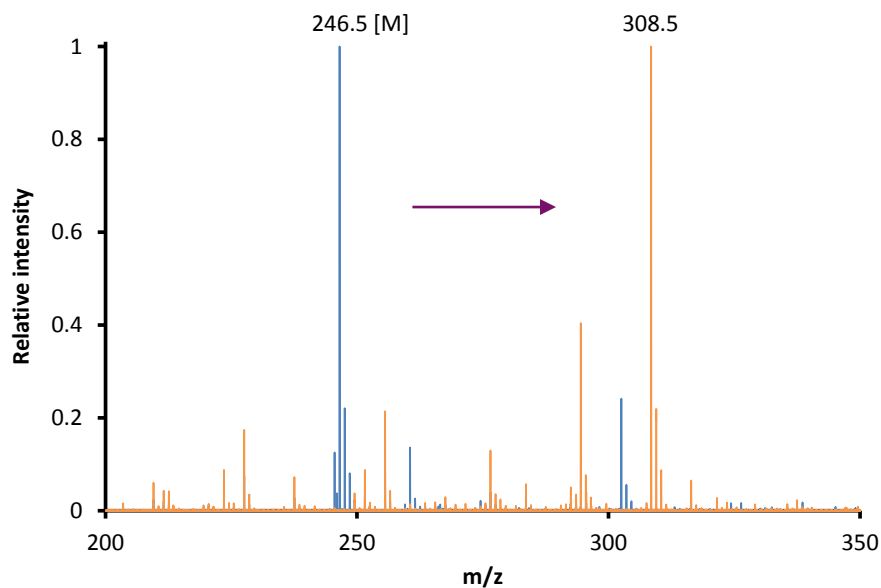
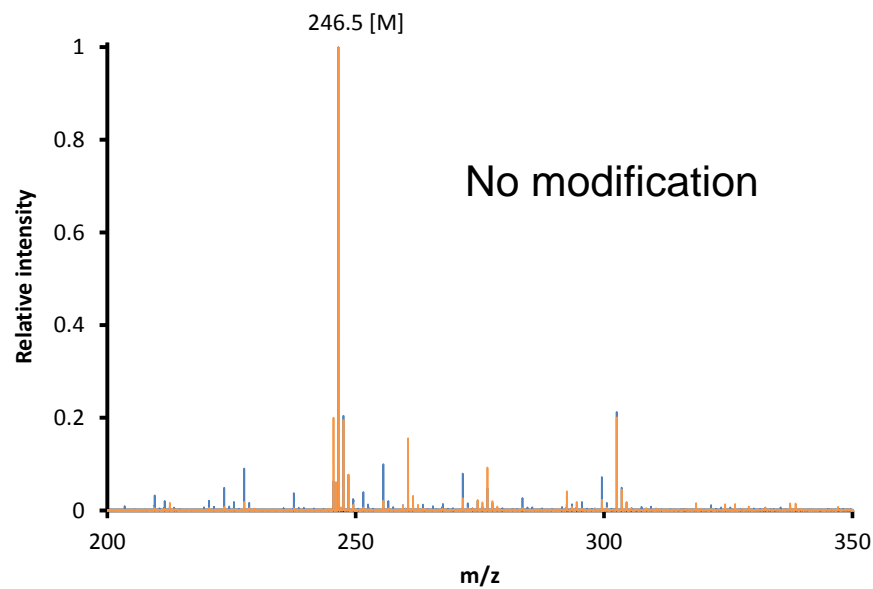


The C-S bond is robust in nitric acid medium

## ESI-MS Study



Free molecule

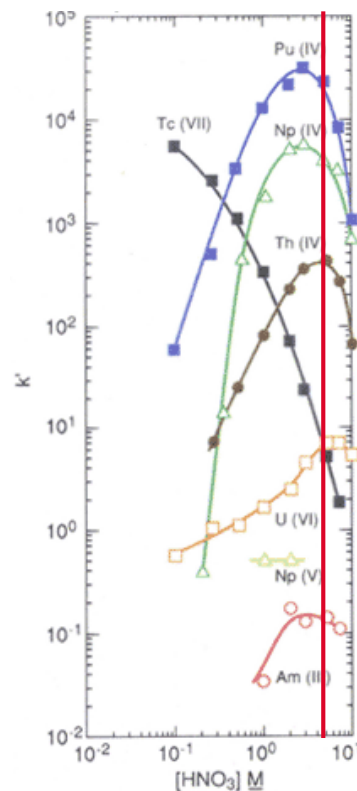
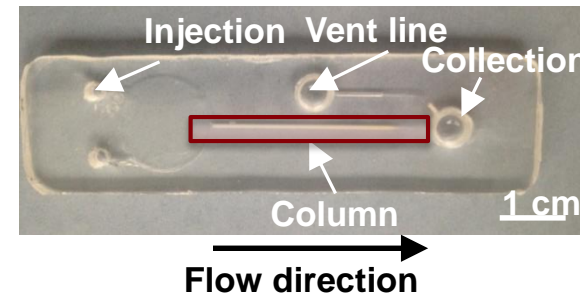
Free molecule after 24 h  
in nitric acid solution $[HNO_3] = 8 \text{ mol.L}^{-1}$  $[HNO_3] = 5 \text{ mol.L}^{-1}$

## Summary of the presented results

- A stationary phase for radiochemical analysis in hard acidic medium was developed
- A robust and versatile method of functionalization was proposed
- The C-S bond formed via thiol-ene chemistry is strong enough to be used in strong nitric acid medium
- The ammonium thiol presents sufficient resistance to be used in  $[\text{HNO}_3] = 5 \text{ mol.L}^{-1}$  medium

## Outlook

- Transfert of the optimized monolith in the COC microsystem
- Radiochemical analysis in 5 M nitric acid medium ?



5 mol.L<sup>-1</sup>

An anion exchange stationary phase : TEVA resin



**cea** **CEA** **PREDICTION OF THE FORMATION OF SEGMENTED FLOW IN MICROSYSTEMS FOR RADIOCHEMICAL LIQUID-LIQUID EXTRACTION**

Vansteene A.<sup>1</sup>, Jamin J.P.<sup>1</sup>, De La Cruz G.<sup>2</sup>, Cavadias S.<sup>2</sup>, Mariet C.<sup>1</sup>, Cote G.<sup>3</sup>

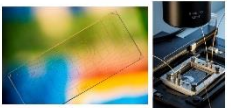
<sup>1</sup> D2M - Service d'Etudes Analytiques et de Mesures des Surfaces (SEAMS), CEA, Université Paris-Saclay, F-91191 Gif sur Yvette, France  
<sup>2</sup> UMR5 - Laboratoire de Chimie des Surfaces (SEAMS), CEA, Université Paris-Saclay, F-91191 Gif sur Yvette, France  
<sup>3</sup> PSL, Chimie ParisTech - CNRS, Institut de Recherche de Chimie Paris, 75005, Paris, France

One of the most important separation techniques in radiochemical procedures is solvent extraction. It involves concentrated acids and corrosive solvents that require microsystems built with robust materials. In the last decade, a growing interest in its use in microsystems has emerged because such systems allow a good control of both the interface area between aqueous and organic phases, and the contact time of the two phases. After a study of parallel flow [1], our goal is to understand and compare the formation of segmented flow for T, flow focusing, and co-flow junctions, and to predict the optimal design in order to enhance solvent extraction.

**OVERVIEW**

**Advantages of microsystems**

- Volume reduction (from mL to  $\mu$ L)
- Low operators' exposure to chemicals
- radiations
- Short analysis time
- High efficiency
- Cost reduction



**DROPLET MICROFLUIDICS**

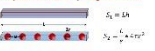
Unlike parallel flows, droplets' mass transfer kinetics are involving both diffusion and convection

- Enhance the surface accessibility for mass transfer to happen by using droplets with a small spacing in between
- Improve mass transfer physically by recirculating species inside droplets

**Limitation of parallel flow:**

- Interface area cannot be easily scaled
- Liquid-liquid extraction controlled only by diffusion
- Not suitable for low kinetic systems.

1. Enhance the surface accessibility for mass transfer to happen by using droplets with a small spacing in between



2. Improve mass transfer physically by recirculating species inside droplets




Fig. 1 - Interface area comparison between parallel flow and droplet-based microfluidics

**DROPLET LIFETIME**

- Inlet : droplets are created by intersecting a continuous and a dispersed phase at a junction
- Outlet : phases are separated by taking advantage of the different affinity of the two phases towards hydrophobic materials

**1 DROPLET GENERATION**

- Very common geometry
- Allow high throughput (1000 Hz) and monodispersity (1% size dispersion)
- Allow discrete volumes (i.e. volume quantization)
- Access to any droplet volume (i.e. sub-pico to  $\mu$ L)
- Very high throughput droplet generation (up to kHz)
- Difficult to form tiny droplets (smaller than channel size)
- Polyspecificity
- Sensitive droplets
- Insertion of a small capillary in corner one
- High drop volume
- Sensitive droplets


**2 DROPLET COALESCENCE**

- Easy way to separate phases
- Based on wettability
- Differences of the two solvents (solvent separation mechanism)
- Based on repulsion of capillary forces on selected materials
- Efficient phase separation
- Commonly used as soft-soft separation device
- Suitable for milliflows
- Extensive microfluidic control techniques and controlled generation (volume accuracy required)
- Easy and most suitable way to get parallel flow via droplet coalescence
- Robustness due to the wettability nature of the functionalization

Parameters affecting flow regime, droplet, droplet size, frequency and spacing

- Viscosities, flow rates of both continuous and dispersed phases
- Interfacial tension between the two phases
- Geometry and dimensions of the junction

**MODELLING**



The size of droplets and their generation rate are shown to be key parameters for liquid-liquid extraction optimization. Microsystems design is therefore investigated in order to determine the operating conditions to control the size and frequency of the droplets, and eventually test microsystems prototyping for specific liquid-liquid extractions.

Modelling is an essential asset for rapid prototyping of microsystems in expensive materials resistant to acids and corrosive solvents used in radiochemistry.

Fig. 2 - Influence of the interface area on the interfacial area between the two phases. The interface area between the two phases is always greater for droplet-based microfluidics than parallel flows (1-3 times higher when optimized).

W. Vansteene et al., *Chem. Sci.*, 2016, 7, 1075-1084.

In droplet-based microsystems, the increase in interfacial area and the internal circulation stimulated within the droplets by their passage along the channel are responsible for a large enhancement in the interfacial mass transfer. Both diffusion and convection have an impact on mass transfer, while diffusion was the only means for parallel flows. Therefore, an improvement in liquid-liquid extraction yield might be expected using segmented instead of parallel flows.

RANC - Budapest, April 10-15, 2016

# THANKS FOR YOUR ATTENTION



## ← Poster of co-workers : an other example of the interest of microfluidics (Ref number : 454)

Commissariat à l'énergie atomique et aux énergies alternatives  
 Centre de Saclay | 91191 Gif-sur-Yvette Cedex  
 DEN/DANS/DPC/SEARS/LANIE – Bât. 391 – PC 33  
 T. +33 (0)1 69 08 83 85 | F. +33 (0)1 69 08 54 11

Direction de l'énergie nucléaire  
 Direction déléguée aux activités nucléaires de Saclay  
 Département de physico-chimie  
 Service d'études analytiques et de réactivité des surfaces  
 Laboratoire de développement analytique nucléaire, isotopique et élémentaire

Etablissement public à caractère industriel et commercial | RCS Paris B 775 685 019