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M. Losno, R. Brennetot, C. Mariet, I. Ferrante, S. Descroix. Microfluidic Systems for Radiochemistry Synthesis and Functionalization of Polymer Monoliths for Chromatographic Separation of U and Eu. ATALANTE 2016 - Nuclear chemistry for sustainable fuel cycles, Jun 2016, Montpellier, France. cea-02509725

HAL Id: cea-02509725

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Submitted on 17 Mar 2020

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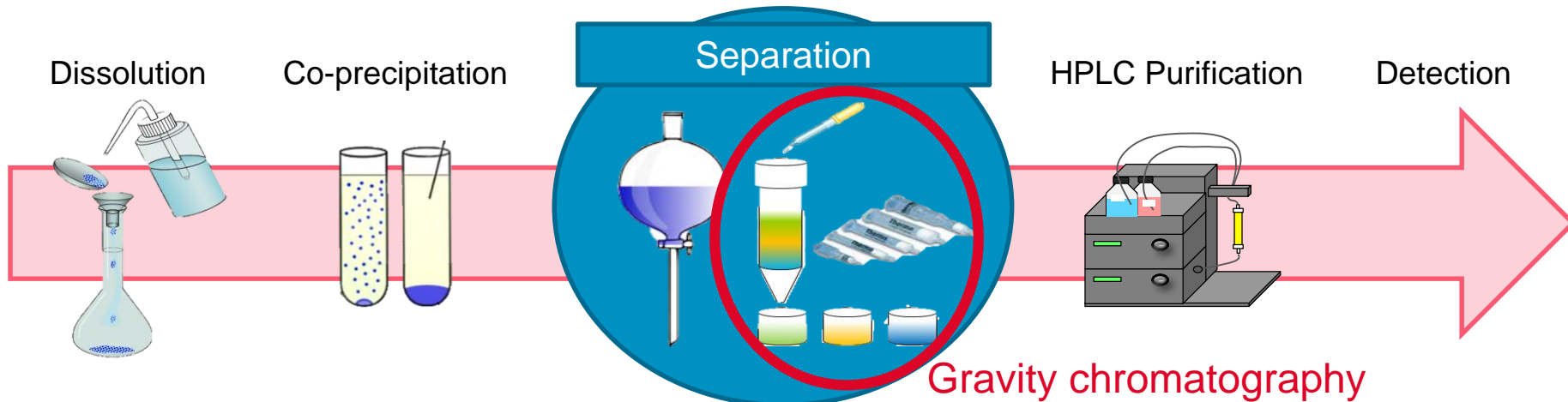


MICROFLUIDIC SYSTEMS FOR RADIOCHEMISTRY: SYNTHESIS AND FUNCTIONALIZATION OF POLYMER MONOLITHS FOR CHROMATOGRAPHIC SEPARATION OF U AND EU

ATALANTE 2016 | Marion Losno

June 9th, 2016





- 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

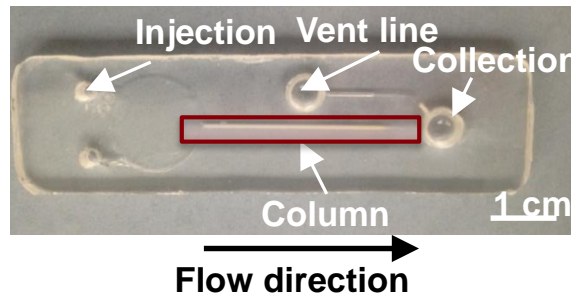


 How to develop this type of technology ?

- 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

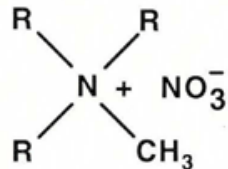
■ Nitric acid resistance

- 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 (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]

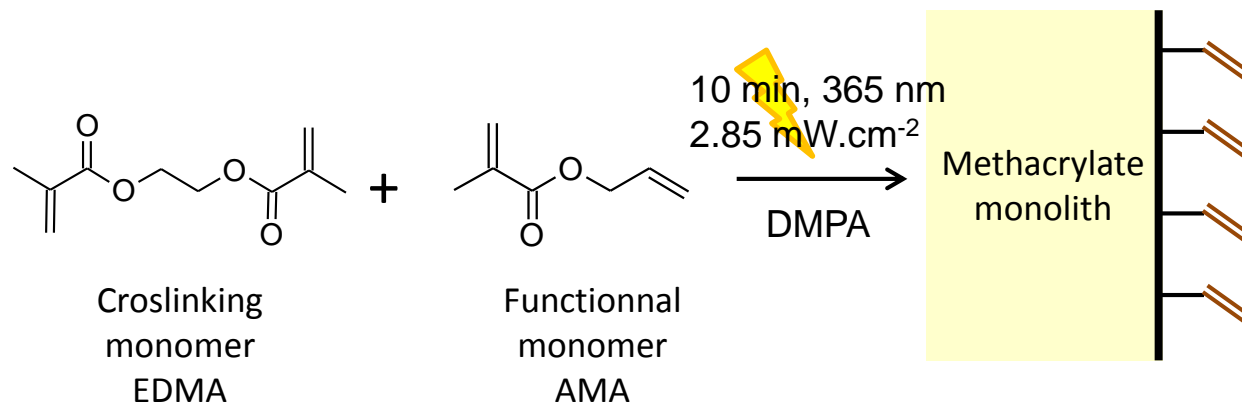
- Photosynthetizable
- Localized
- Chemical resistance
- Mechanical resistance
- Low flow resistance

- Choice of thiolene « click chemistry » [2]

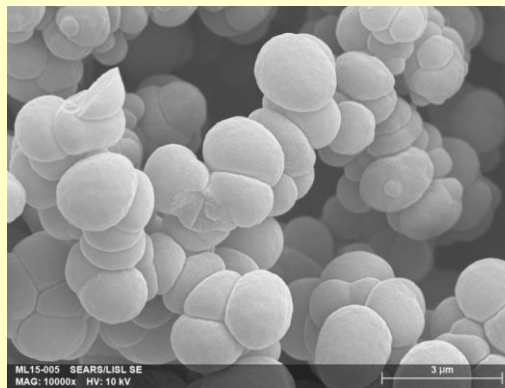
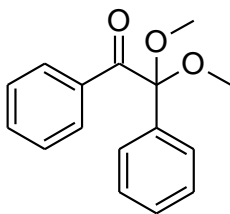
- Photochemical reaction
- Localized
- Chemical resistance
- Versatility

[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 $\approx 1 \mu\text{m}$

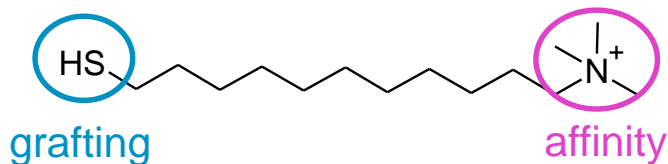
Permeability $\approx 10^{-14} \text{ m}^2$

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

Total porosity $\approx 60 \%$

Choice of molecules

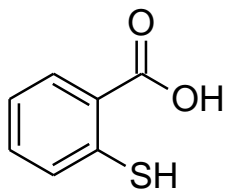
- Molecule to be grafted : ammonium thiol



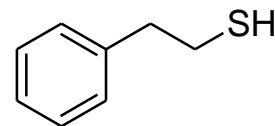
- 😊 Commercially available
- 😞 Price
- 😞 Characterization

→ Study of the reaction through different molecules

Thiosalicylic acid

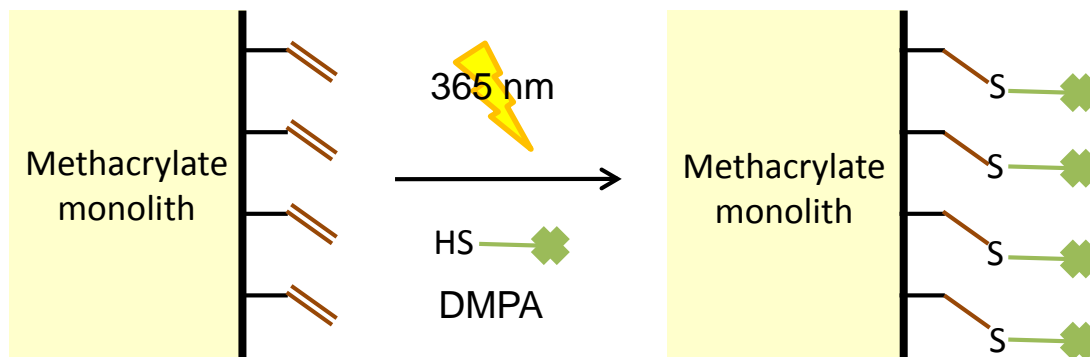


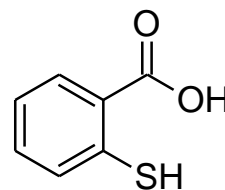
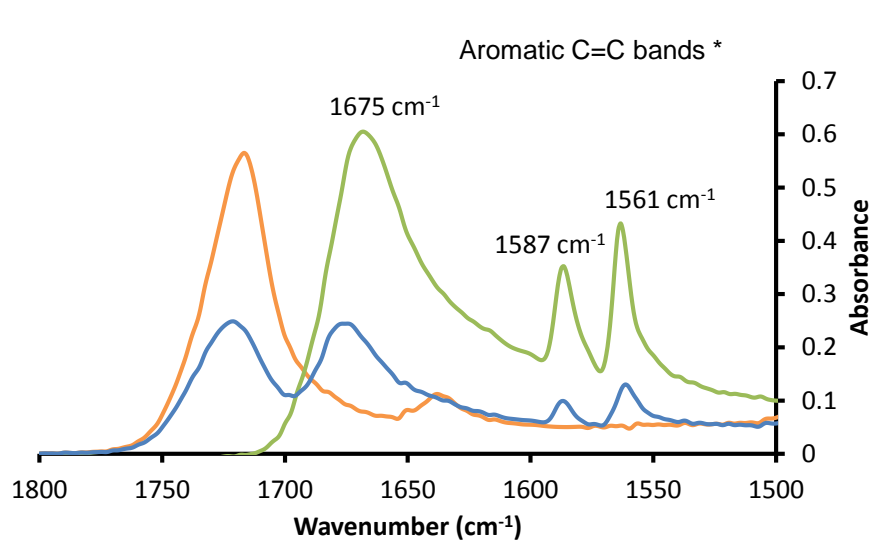
- 😊 Commercially available
- 😊 Price
- 😊 Characterization



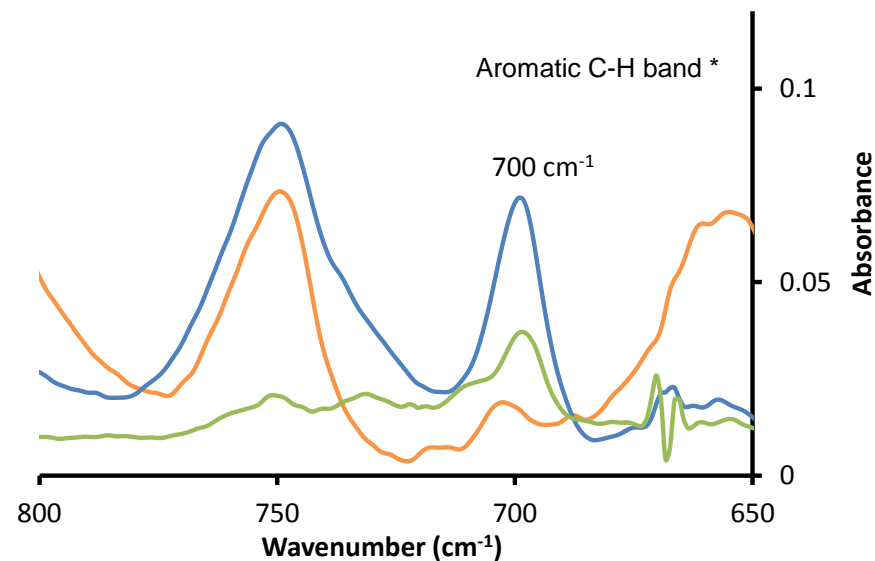
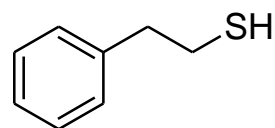
2-phenylethanethiol

Procedure





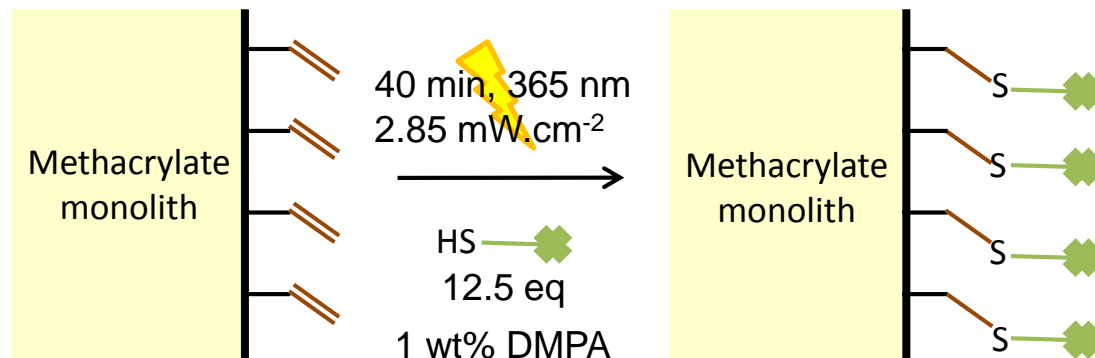
Blank monolith
Thiol
Grafted monolith



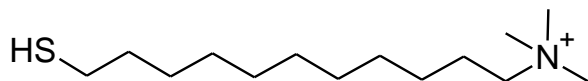
* Skoog, D. A., D. M. West and F. J. Holler (1997). *Chimie analytique*. Bruxelles, Boeck and Larcier.

* Silverstein, Basler and Morill (1998). *Identification spectrométrique de composés organiques*, Boeck and Larcier.

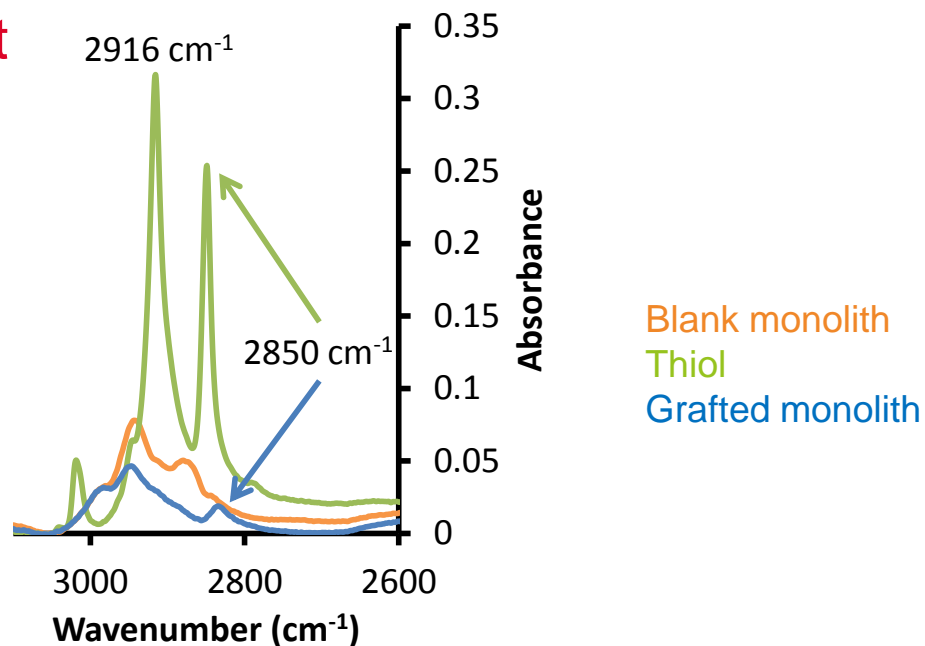
Optimized conditions



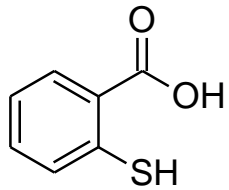
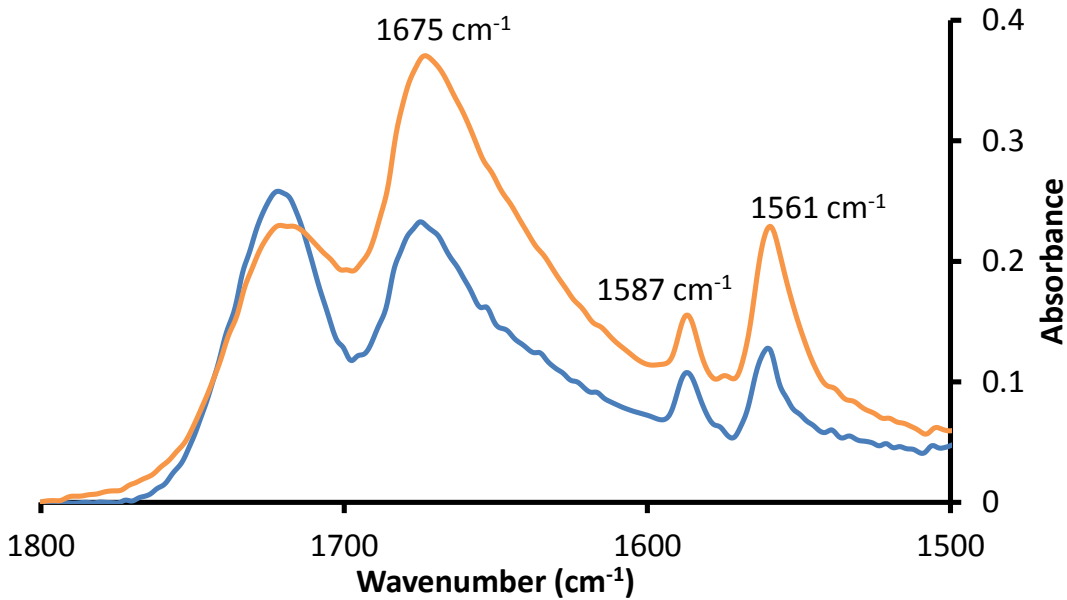
Molecule of interest



Versatile functionalization

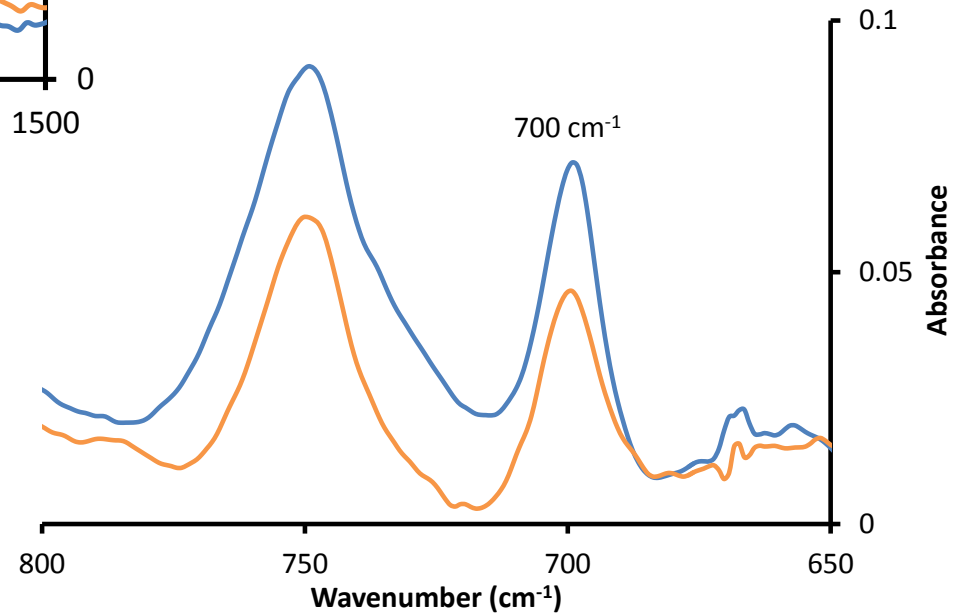
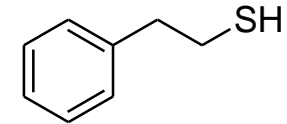


CHEMICAL RESISTANCE OF THE FORMED C-S BOND



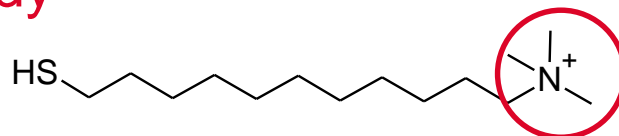
Grafted monolith

Grafted monolith after 24 h in a 8 mol.L⁻¹ nitric acid aqueous solution

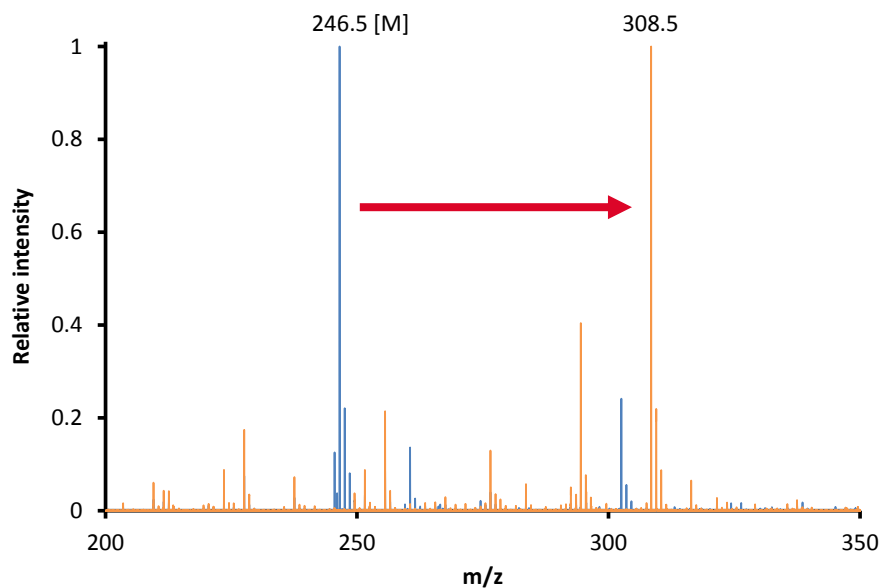
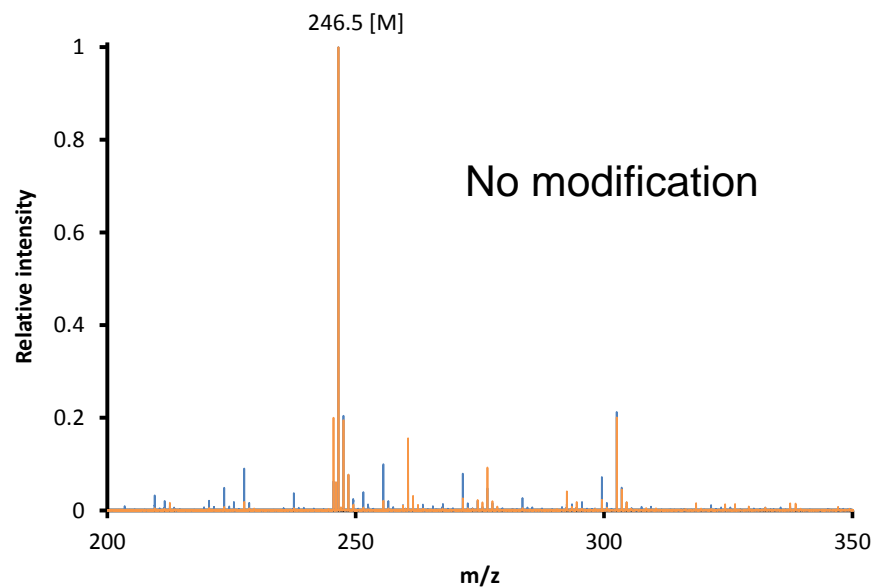


The C-S bond is robust in nitric acid medium

ESI-MS Study



Free molecule

Free molecule after 24 h
in nitric acid solution $[\text{HNO}_3] = 8 \text{ mol.L}^{-1}$  $[\text{HNO}_3] = 5 \text{ mol.L}^{-1}$

* Losno, M. et al (2016). "Photochemical synthesis and versatile functionalization method of a robust porous poly(ethylene glycol methacrylate-co-allyl methacrylate) monolith dedicated to radiochemical separation in a centrifugal microfluidic platform." *Micromachines* **7**(3): 45.

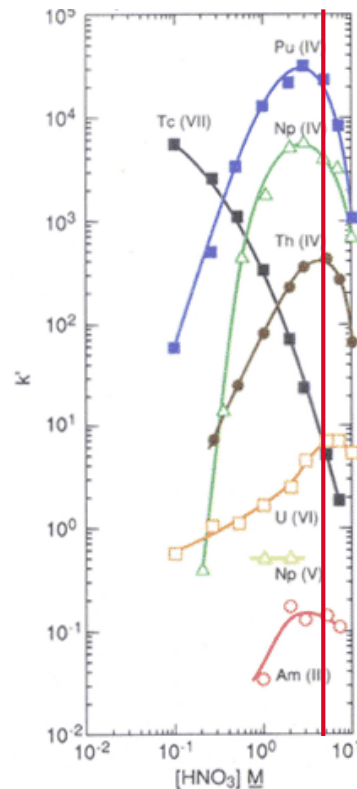
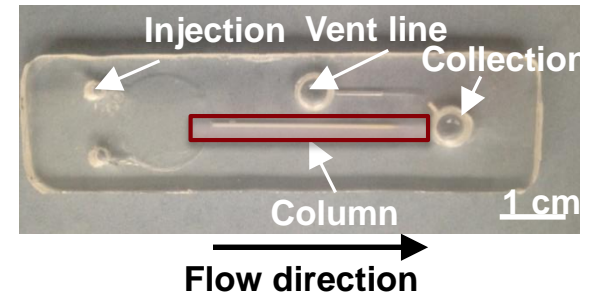
* Losno, M. et al (2016). "Microsystems for Anion Exchange Separation of Radionuclides in Nitric Acid Media" *Procedia chemistry*

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⁻¹

An anion exchange stationary phase : TEVA resin

THANKS FOR YOUR ATTENTION



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