DE LA RECHERCHE À L'INDUSTRIE

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


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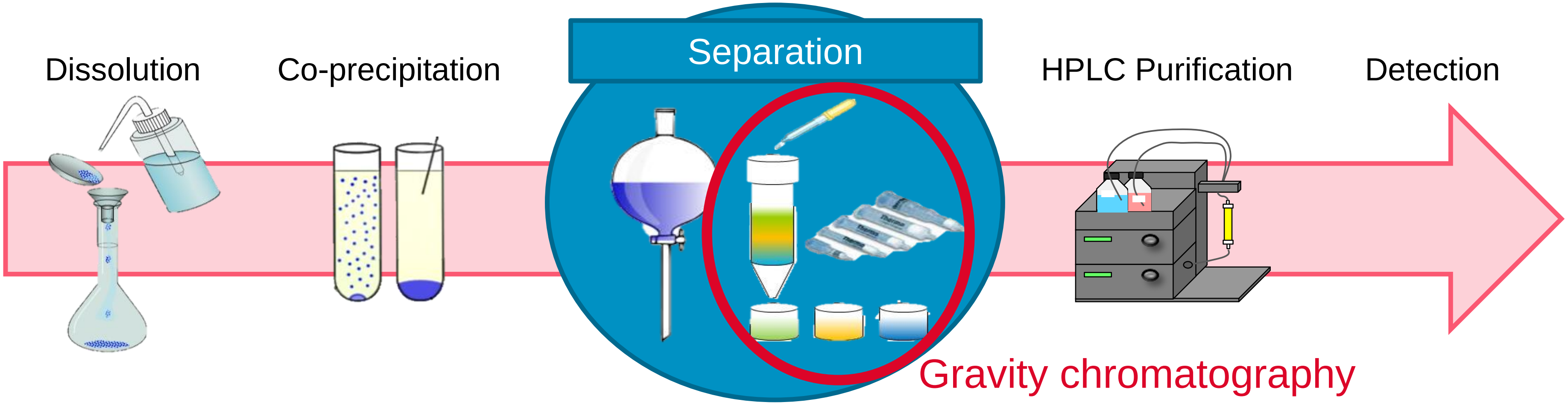
nuclear chemistry for sustainable fuel cycles

# RADIOCHEMICAL ANALYSIS



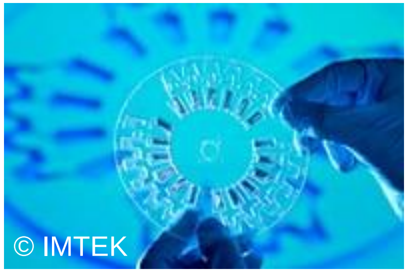

- Many constraints have to be taken into account such as
  - Glove box handling
  - Concentrated irradiant samples
  - Waste management

## ☺ 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 OF PLASTIC MICROSYSTEMS FOR LAB-ON-CD SEPARATION

- 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

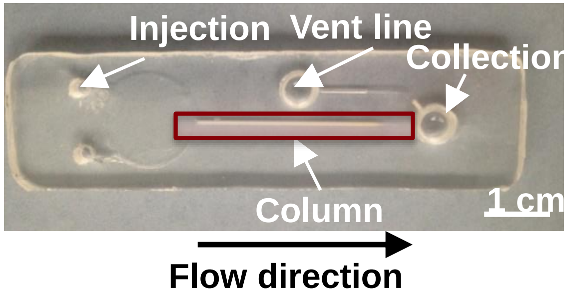



How to develop this type of technology ?

# DEVELOPEMENT OF A LAB-ON-CD SYSTEM

- 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

* Bruchet, A. et al. (2013). "Centrifugal microfluidic platform for radiochemistry: potentialities for the chemical analysis of nuclear spent fuels." Talanta **116**: 488-494.

# RADIOCHEMICAL SEPARATIONS

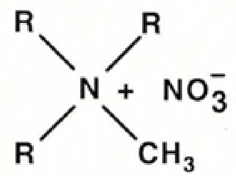
- Constraints due to the analysis

  - Nitric acid resistance
    - Corresponding to the dissolution medium of radiochemical samples

    When $[HNO_3] > 4 mol.L^{-1}$ *

    - Formation of $[UO_2(NO_3)_x]^{(2-x)}$ ($1 \leq x \leq 3$) anionic complex
    - Cationic form of lanthanides ($Ln^{3+}$)

  - Functionalization by an anion exchanger will enable the separation of the two components in $[HNO_3] > 4 mol.L^{-1}$




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.

# WHY PHOTOCHEMICAL SYNTHESIS ?

- Stationnary phase constraints
  - Easy to synthetize
  - Localization of the phase

} ☺ Photochemistry

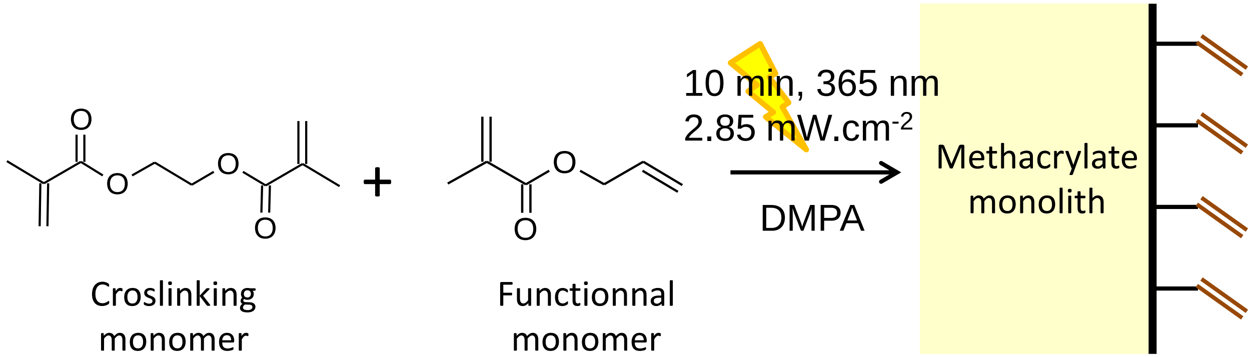
Sationnary phase = polymer + grafting of a molecule of interest

- Choice of oragnic 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.

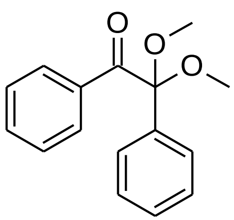
# ORGANIC MONOLITH SYNTHESIS OPTIMIZATION AT MACROSCALE

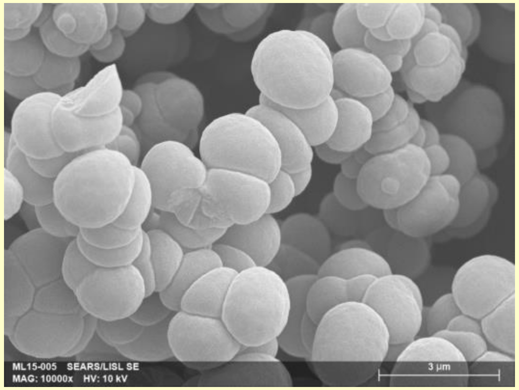



Croslinking monomer EDMA

Functionnal monomer AMA

- 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 ≈ 1 µm

Permeability ≈ $10^{-14}$ $m^2$

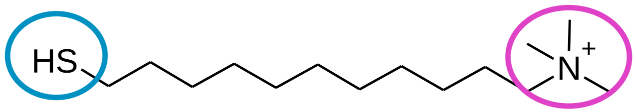
Density ≈ 0.4 $g.mL^{-1}$

Total porosity ≈ 60 %

# FUNCTIONALIZATION BY CLICK-CHEMISTRY AT MACRO SCALE

## Choice of molecules

- Molecule to be grafted : ammonium thiol

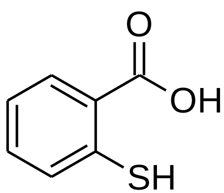



grafting affinity

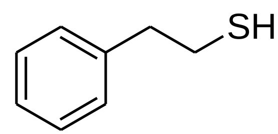
☺ Commercially available
☹ Price
☹ Characterization

→ Study of the reaction through different molecules

Thiosalicylic acid

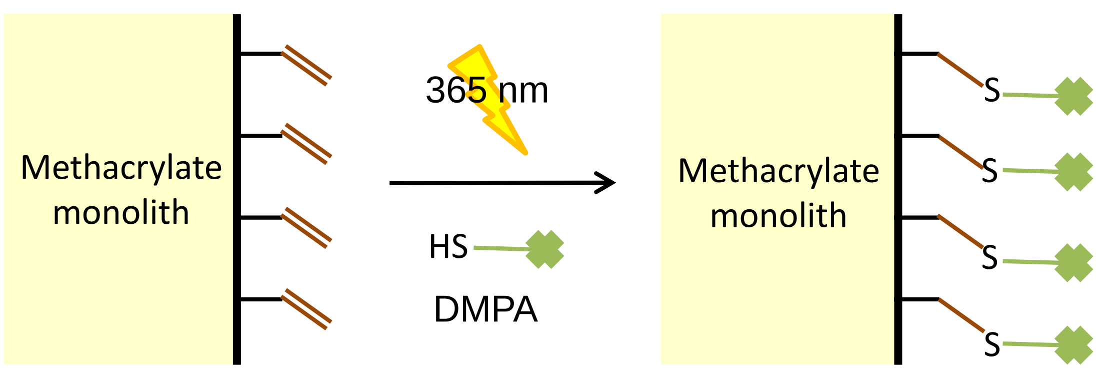



☺ Commercially available
☺ Price
☺ Characterization

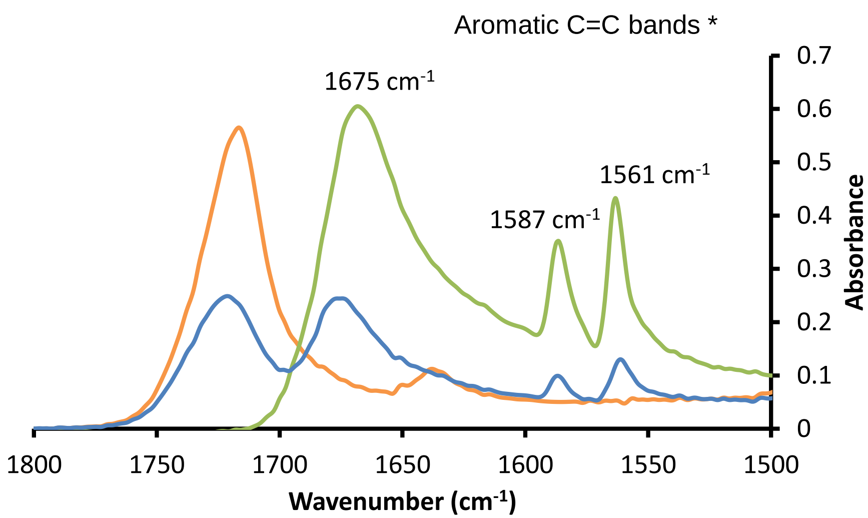


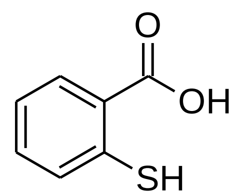

2-phenylethanethiol

## Procedure

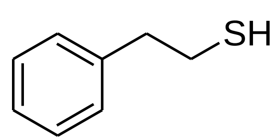


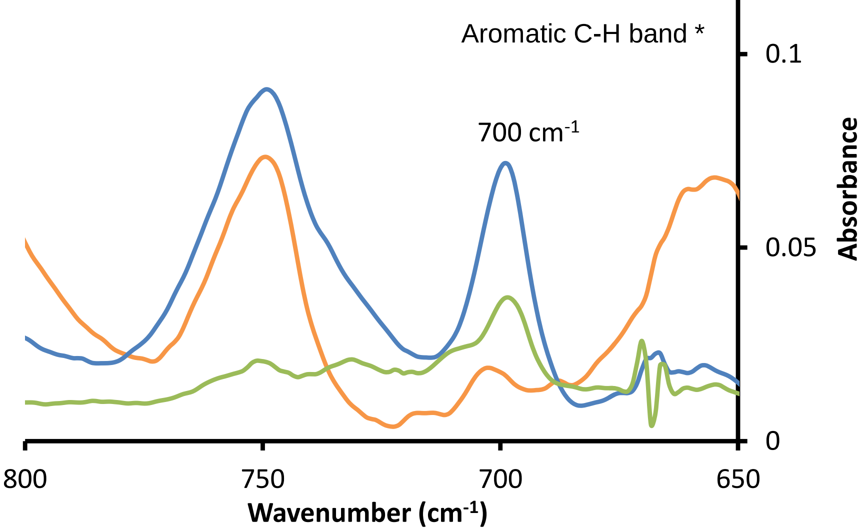
# VERSATILITY OF FUNCTIONALIZATION




Blank monolith
Thiol
Grafted monolith



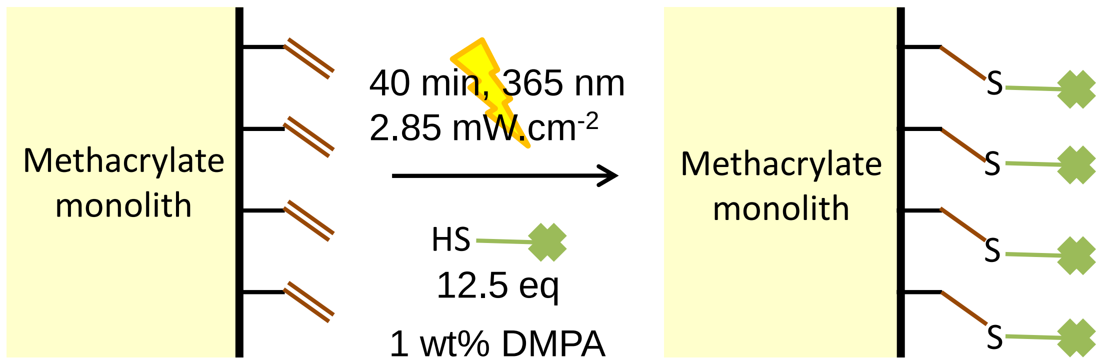





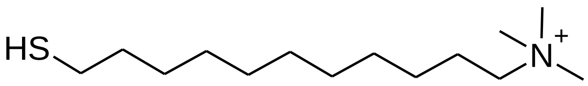

* Skoog, D. A., D. M. West and F. J. Holler (1997). Chimie analytique. Bruxelles, Boeck and Larcier.
* Silverstein, Basler and Morill (1998). Identification spectrométrique de composés organiques, Boeck and Larcier.

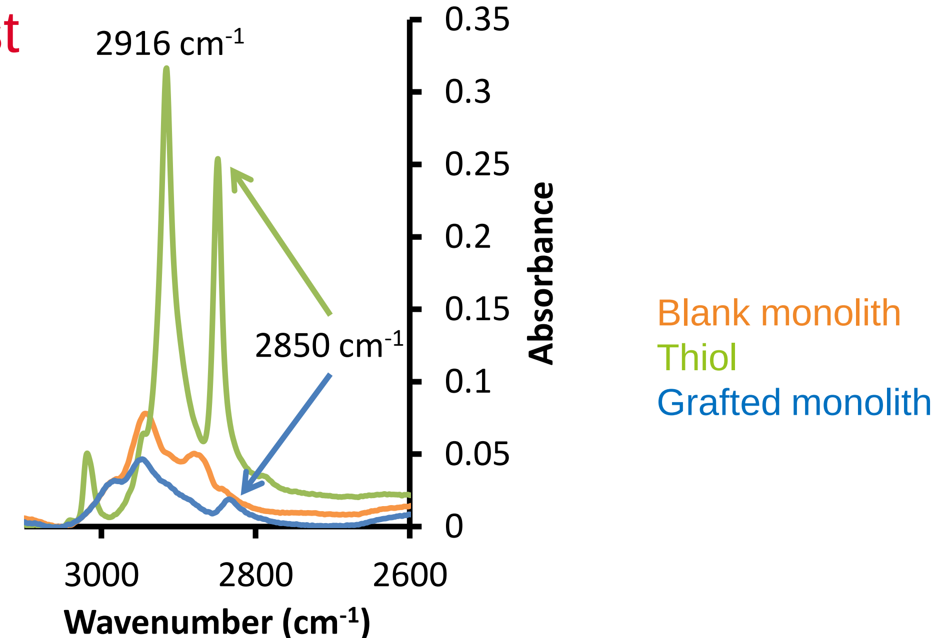
# VERSATILITY OF FUNCTIONALIZATION

## Optimized conditions




## Molecule of interest

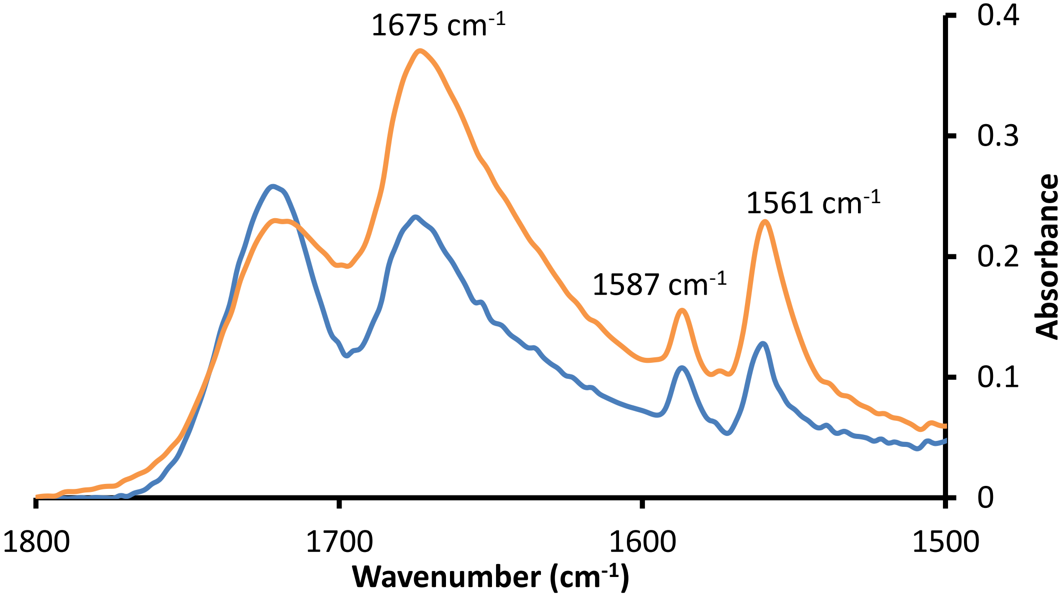



**Versatile functionalization**

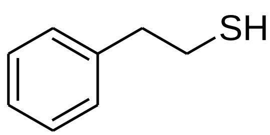

* Skoog, D. A., D. M. West and F. J. Holler (1997). Chimie analytique. Bruxelles, Boeck and Larcier.
* Silverstein, Basler and Morill (1998). Identification spectrométrique de composés organiques, Boeck and Larcier.

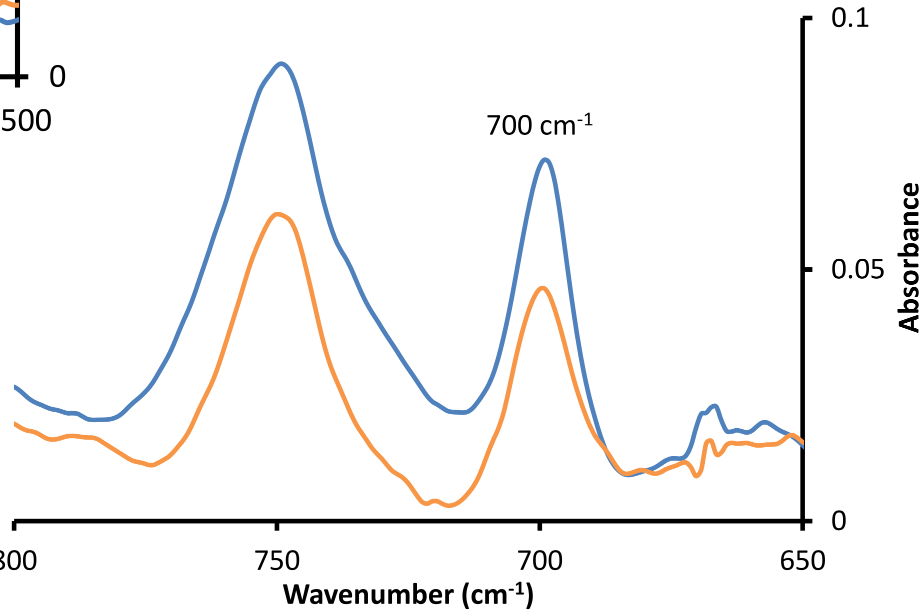
# CHEMICAL RESISTANCE OF THE FORMED C-S BOND

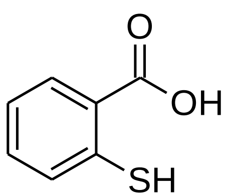



Grafted monolith

Gafted monolith after 24 h in a 8 mol.L$^{-1}$ nitric acid aqueous solution



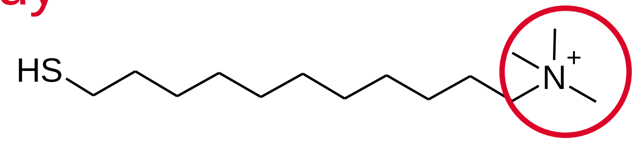




The C-S bond is robust in nitric acid medium

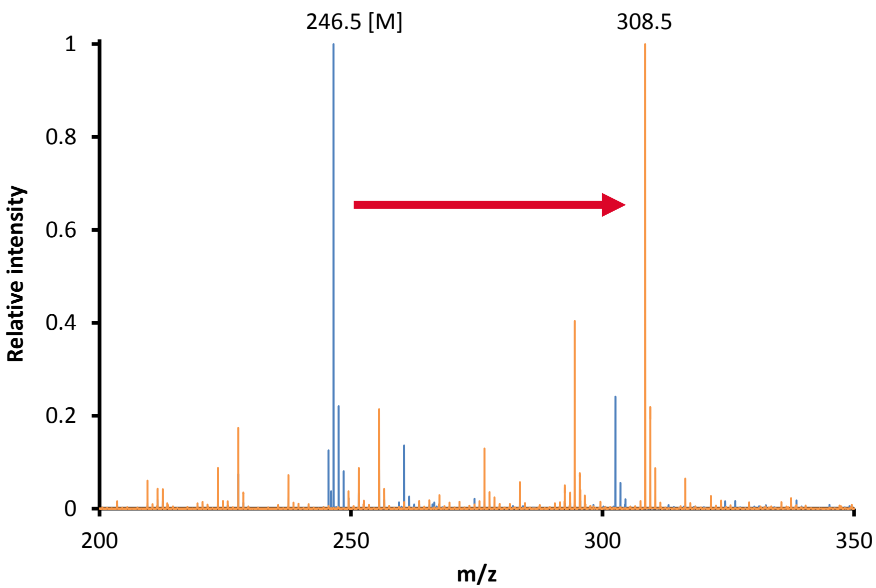
# AMMONIUM THIOL RESISTANCE

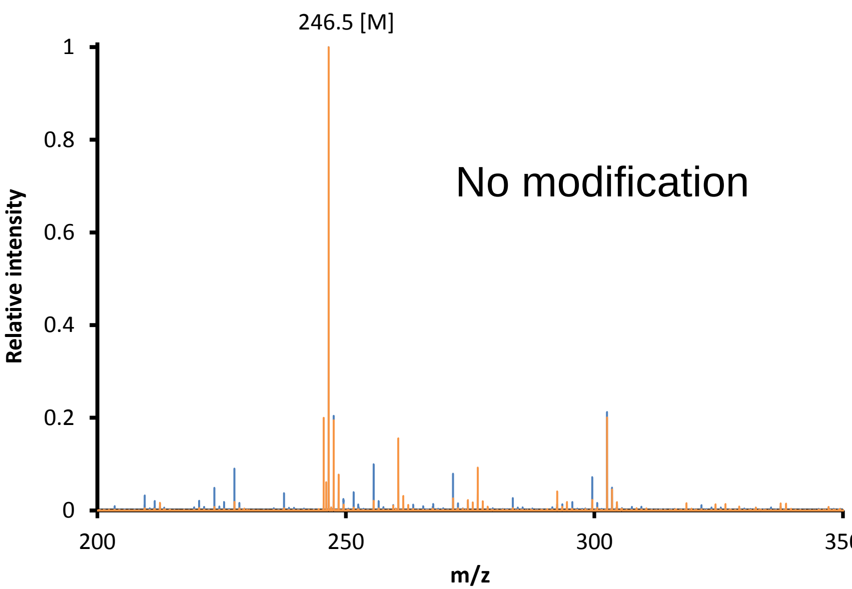
## ESI-MS Study




Free molecule

Free molecule after 24 h in nitric acid solution




$[HNO_3] = 8\ mol.L^{-1}$

$[HNO_3] = 5\ mol.L^{-1}$

* 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

# CONCLUSION

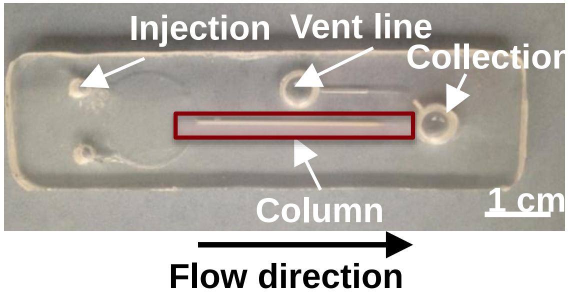
## Summary of the presented results

- 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 $[HNO_3] = 5\ mol.L^{-1}$ medium

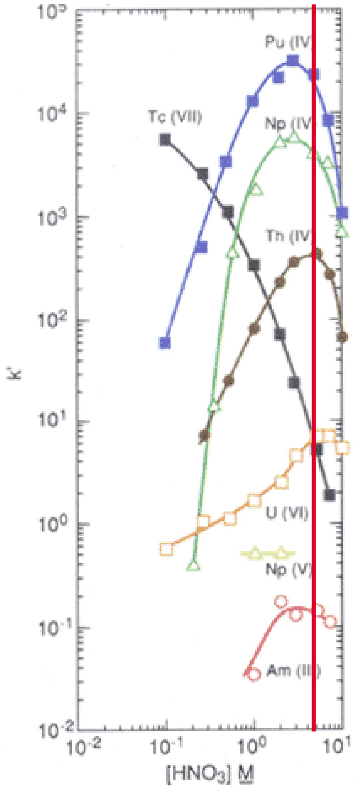
# CONCLUSION

## 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 stationnary phase : TEVA resin

# THANKS FOR YOUR ATTENTION

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