

Anion exchange microsystems for radionuclides separation in nitric acid media

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ANION EXCHANGE MICROSYSTEMS FOR RADIONUCLIDES SEPARATION IN NITRIC ACID MEDIA

Marion Losno, René Brennetot, Clarisse Mariet [1]

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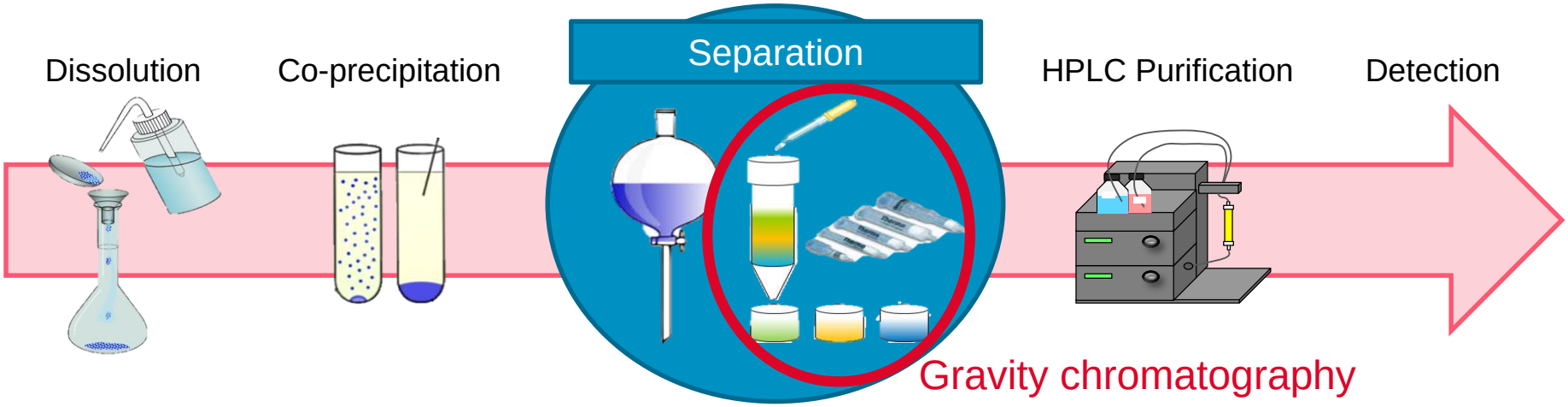
Ivan Ferrante, Stéphanie Descroix [2]

[2] MMBM Group, Institut Curie Research Center, CNRS UMR 168, Paris, France

April 12th, 2016

RANC April 10-15, 2016 Budapest, Hungary
1st International Conference on Radioanalytical and Nuclear Chemistry

RADIOCHEMICAL ANALYSIS



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

MICROSYSTEMS FOR ANALYSIS IN THE NUCLEAR FIELD

☺ Benefits of miniaturization

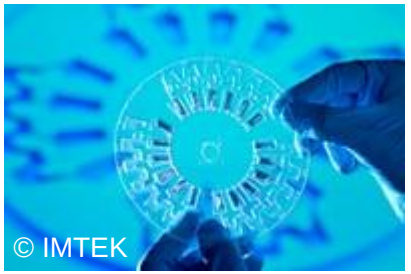
- A little amount of sample needed for the analysis
  - Decrease of the volume handled by the operators
  - Decrease of the dose received
  - Decrease of the amount of waste produced -> reduces analysis cost





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



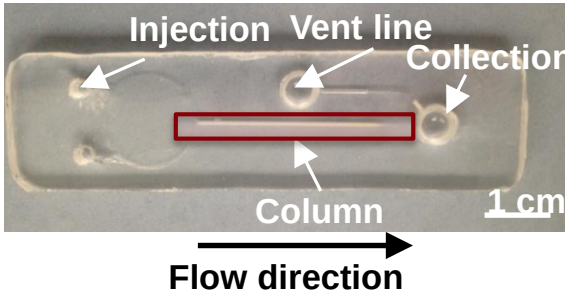
→ How to develop this type of technology ?

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

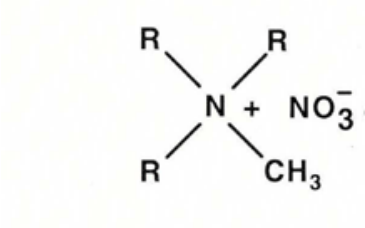
* Bruchet, A. et al. (2013). "Centrifugal microfluidic platform for radiochemistry: potentialities for the chemical analysis of nuclear spent fuels." Talanta **116**: 488-494.

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

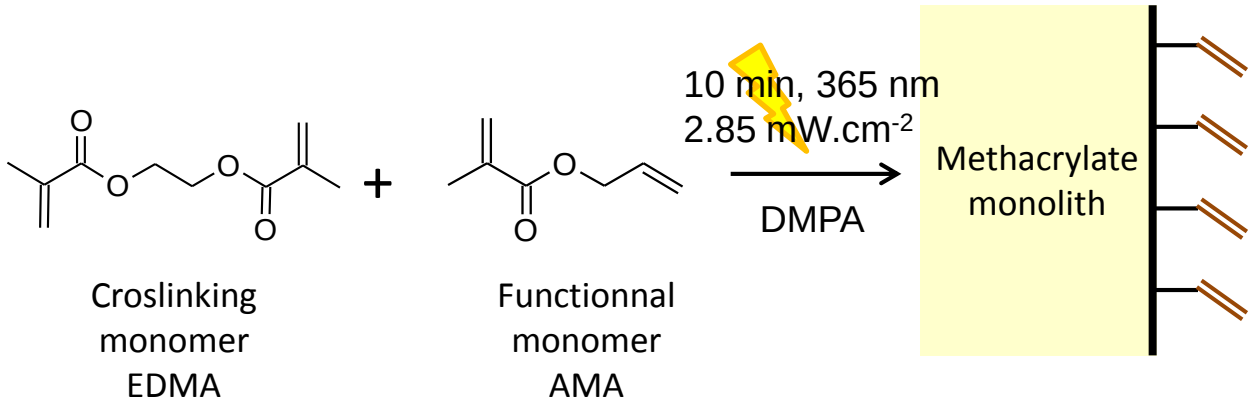
Sationnary phase = polymer + grafting of a molecule of interest

- Choice of oragnic methacrylate monolith [1]
  - Photosynthetizable
  - Localized
  - Chemical resistance
  - Mechanical resistance
  - Low flow resistance

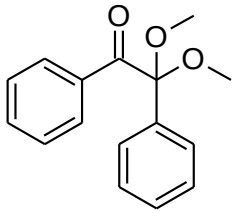
- Choice of thiolene « click chemistry » [2]
  - Photochemical reaction
  - Localized
  - Chemical resistance
  - Versatility

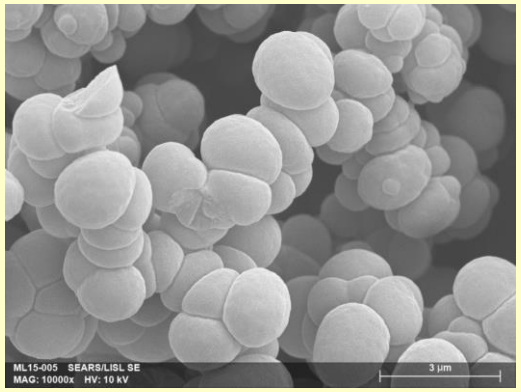
[1] Svec, F. and J. M. J. Fréchet (1996). "New designs of macroporous polymers and supports: From separation to biocatalysis." Science **273**(5272): 205-211.
[2] Kolb, H. C., M. G. Finn and K. B. Sharpless (2001). "Click chemistry: Diverse chemical function from a few good reactions." Angewandte Chemie International Edition **40**(11): 2004-2021.

ORGANIC MONOLITH SYNTHESIS OPTIMIZATION AT MACROSCALE



- 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

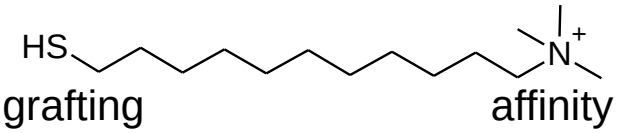
Density ≈ 0.4 $g.mL^{-1}$

Total porosity ≈ 60 %

FUNCTIONALIZATION BY CLICK-CHEMISTRY AT MACRO SCALE

Choice of molecules

- Molecule to be grafted

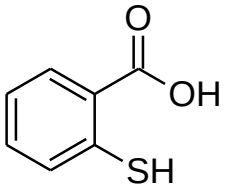


→ Study of the reaction through different molecules

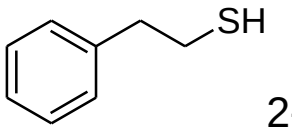
Ammonium thiol

☺ Commercially available
☹ Price
☹ Characterization

Thiosalicylic acid

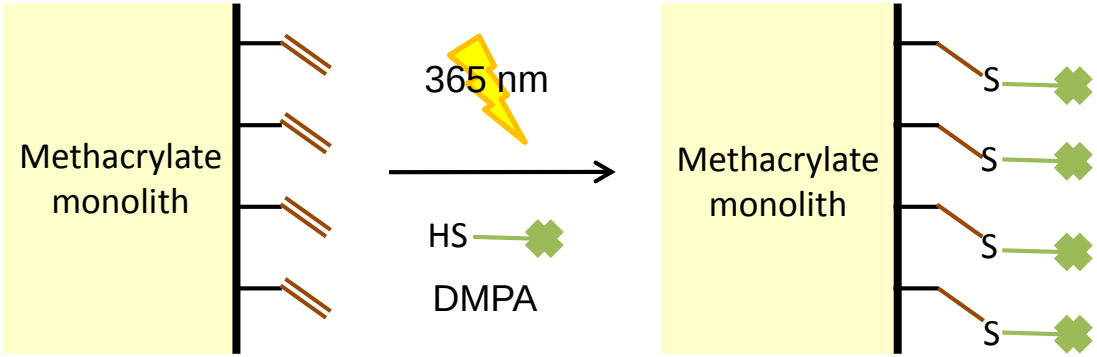


☺ Commercially available
☺ Price
☺ Characterization

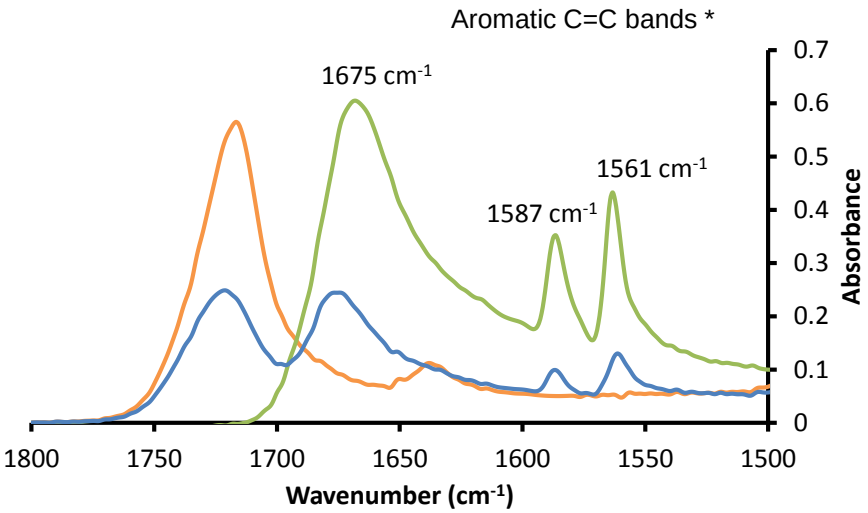


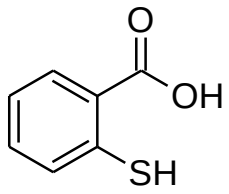
2-phenylethanethiol

Procedure

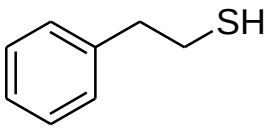


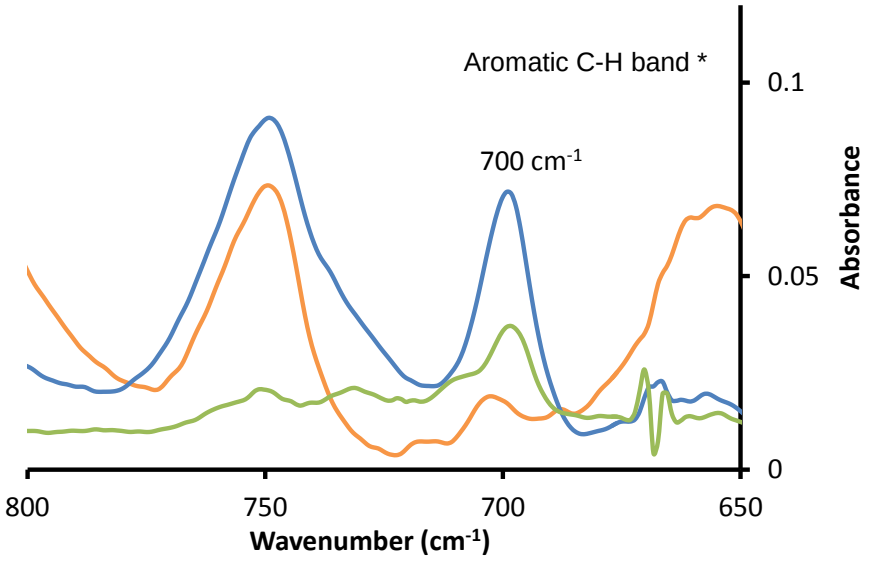
VERSATILITY OF FUNCTIONALIZATION





Blank monolith
Thiol
Grafted monolith

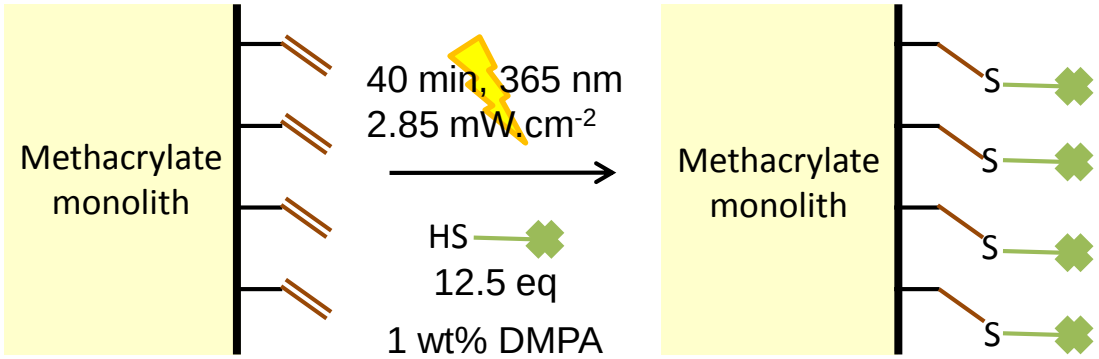




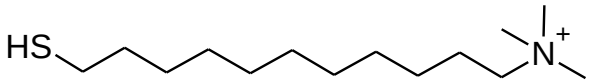
* Skoog, D. A., D. M. West and F. J. Holler (1997). Chimie analytique. Bruxelles, Boeck and Larcier.
* Silverstein, Basler and Morill (1998). Identification spectrométrique de composés organiques, Boeck and Larcier.

VERSATILITY OF FUNCTIONALIZATION

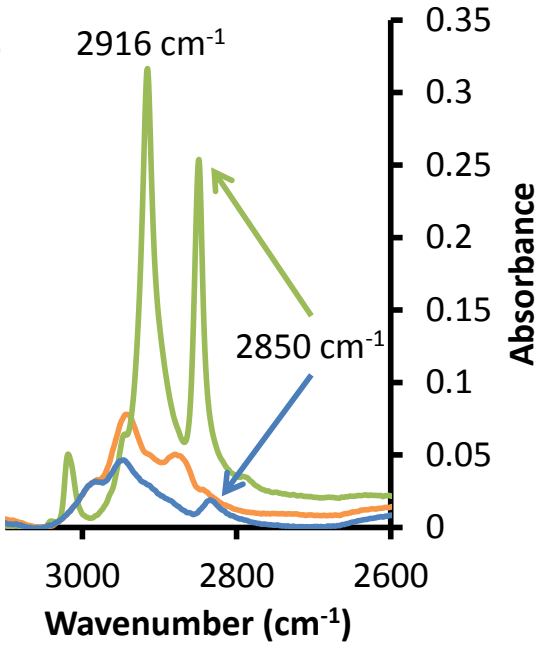
Optimized conditions



Molecule of interest



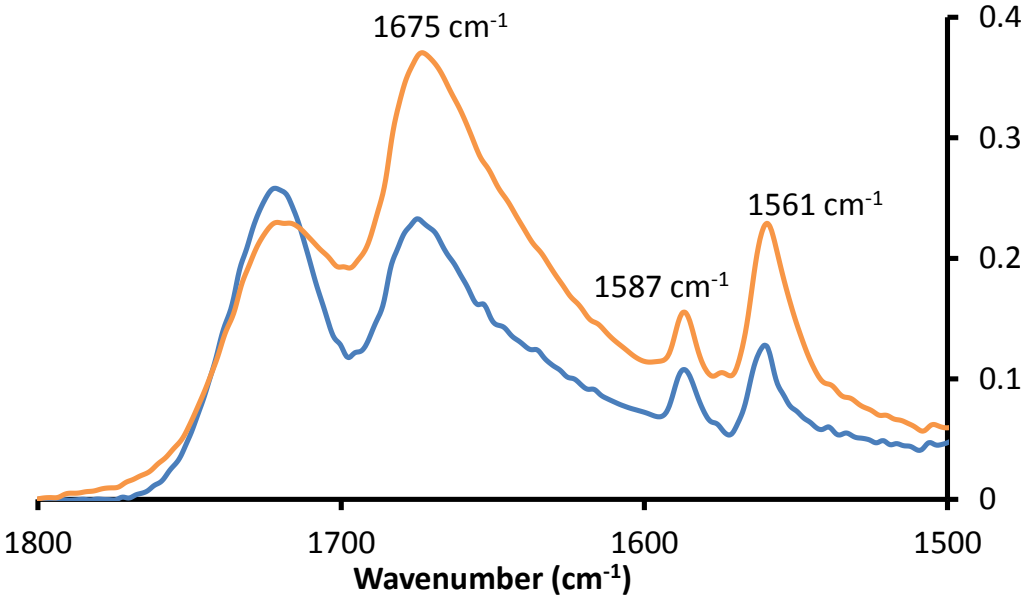
Versatile functionalization



Blank monolith
Thiol
Grafted monolith

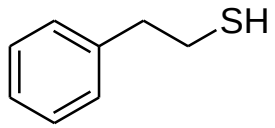
* Skoog, D. A., D. M. West and F. J. Holler (1997). Chimie analytique. Bruxelles, Boeck and Larcier.
* Silverstein, Basler and Morill (1998). Identification spectrométrique de composés organiques, Boeck and Larcier.

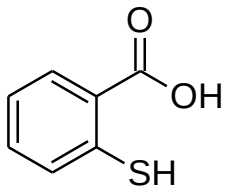
CHEMICAL RESISTANCE OF THE FORMED C-S BOND

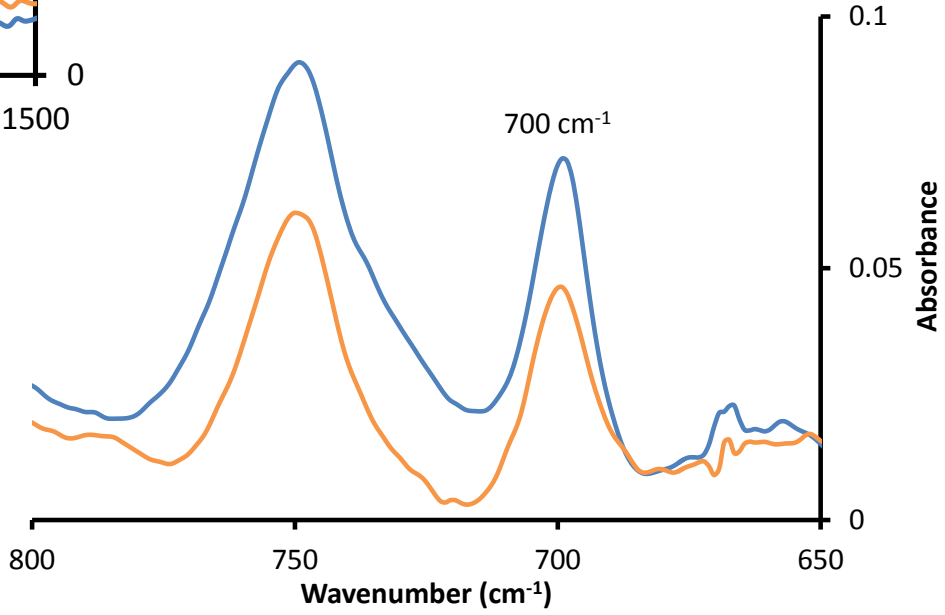


Grafted monolith

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



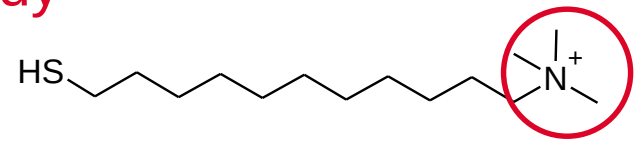




The C-S bond is robust in nitric acid medium

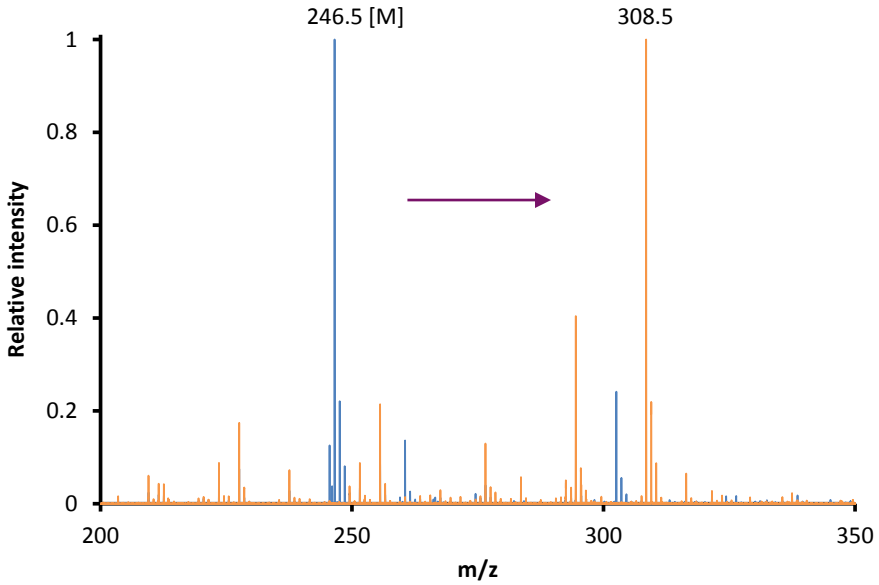
AMMONIUM THIOL RESISTANCE

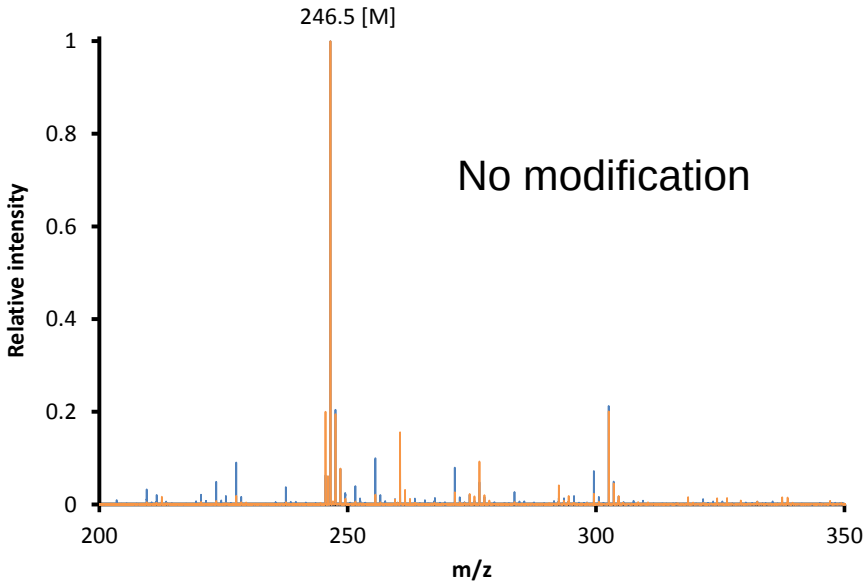
ESI-MS Study



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.

CONCLUSION

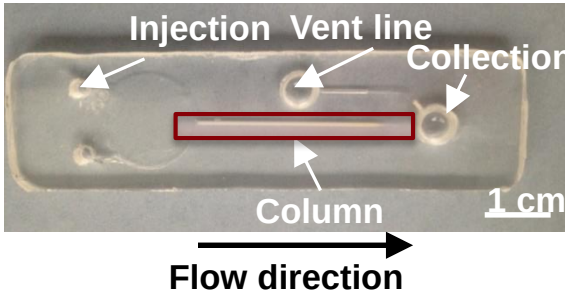
Summary of the presented results

- 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

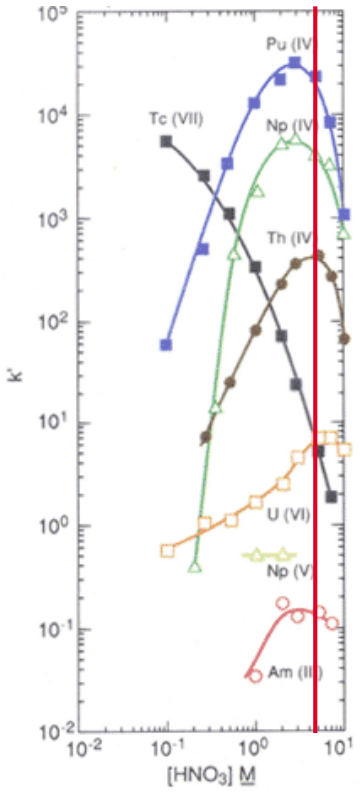
CONCLUSION

Outlook

- Transfert of the optimized monolith in the COC microsystem

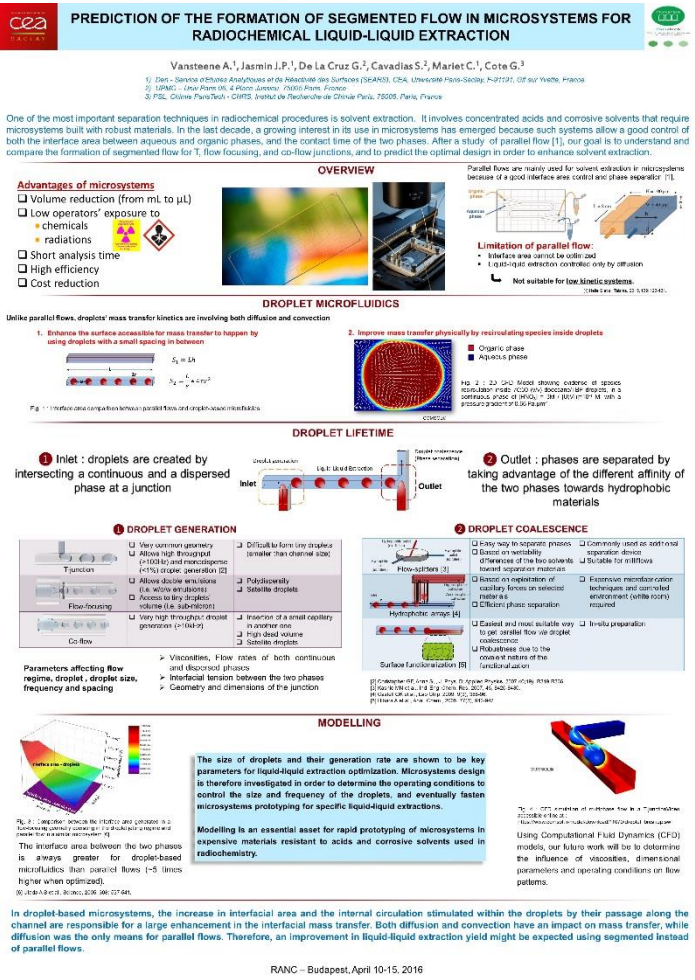


- Radiochemical analysis in 5 M nitric acid medium ?



5 mol.L^{-1}

An anion exchange stationnary phase : TEVA resin



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

Vansteene A.[1], Jasmin J.P.[1], De La Cruz G.[2], Cavadias S.[2], Mariet C.[1], Cote G.[3]

1) Den - Service d'Etudes Analytiques et de Réactivité des Surfaces (SEARS), CEA, Université Paris-Saclay, F-91191, Gif sur Yvette, France
2) UPMC - Univ Paris 06, 4 Place Jussieu, 75005 Paris, France
3) 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 µL)
- Low operators' exposure to
  - chemicals
  - radiations
- Short analysis time
- High efficiency
- Cost reduction

Parallel flows are mainly used for solvent extraction in microsystems because of a good interface area control and phase separation [1].

Limitation of parallel flow:
- Interface area cannot be optimized
- Liquid-liquid extraction controlled only by diffusion

Not suitable for low kinetic systems.

DROPLET MICROFLUIDICS

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

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

$S_1 = 1h$

$S_2 = \frac{L}{2} + \pi r^2$

2. Improve mass transfer physically by recirculating species inside droplets

Organic phase
Aqueous phase

DROPLET LIFETIME

1 Inlet : droplets are created by intersecting a continuous and a dispersed phase at a junction

Inlet

Outlet

2 Outlet : phases are separated by taking advantage of the different affinity of the two phases towards hydrophobic materials

1 DROPLET GENERATION

T-junction	❑ Very common geometry ❑ Allows high throughput (>100 Hz) and monodisperse (<1%) droplet generation [2]	❑ Difficult to form tiny droplets (smaller than channel size)
Flow-focusing	❑ Allows double emulsions (i.e. w/o/w emulsions) ❑ Access to tiny droplets' volume (i.e. sub-nanoliter)	❑ Polydispersity ❑ Satellite droplets
Co-flow	❑ Very high throughput droplet generation (>10 kHz)	❑ Insertion of a small capillary in another one ❑ High dead volume ❑ Satellite droplets

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

2 DROPLET COALESCENCE

Flow-splitters [3]	❑ Easy way to separate phases ❑ Based on wettability differences of the two solvents toward separation materials	❑ Commonly used as additional separation device ❑ Suitable for millifows
Hydrophobic arrays [4]	❑ Based on exploitation of capillary forces on selected materials ❑ Efficient phase separation	❑ Extensive microfabrication techniques and controlled environment (white room) required
Surface functionalization [5]	❑ Easiest and most suitable way to get parallel flow via droplet coalescence ❑ Robustness due to the covalent nature of the functionalization	❑ In-situ preparation

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 fasten 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.

The interface area between the two phases is always greater for droplet-based microfluidics than parallel flows (~5 times higher when optimized).

Using Computational Fluid Dynamics (CFD) models, our future work will be to determine the influence of viscosities, dimensional parameters and operating conditions on flow patterns.

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)

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