

Maintaining parallel flows in microsystem during solvent extraction of concentrated Uranium(VI) solutions a solution for the screening of extractive molecules

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DE LA RECHERCHE À L'INDUSTRIE

MAINTAINING PARALLEL FLOWS IN MICROSYSTEM DURING SOLVENT EXTRACTION OF CONCENTRATED URANIUM(VI) SOLUTIONS: A SOLUTION FOR THE SCREENING OF EXTRACTIVE MOLECULES

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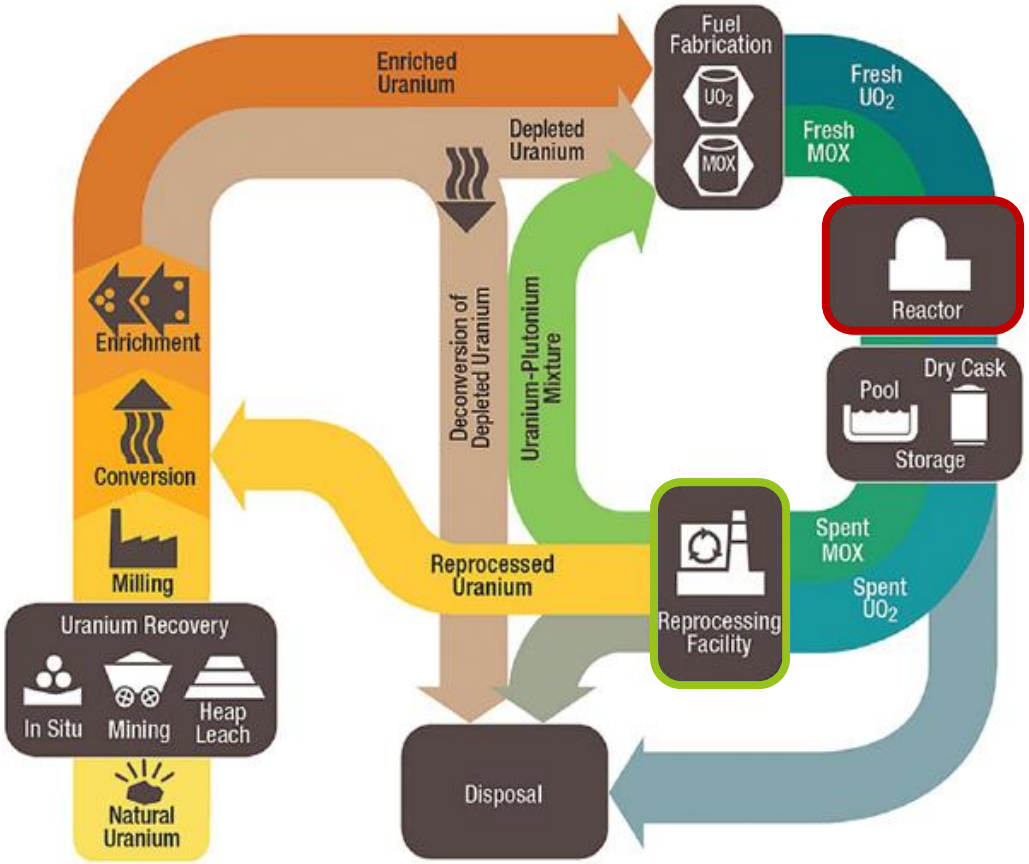
www.cea.fr

PUREX: Plutonium and Uranium Recovery Extraction

Nuclear plant purpose

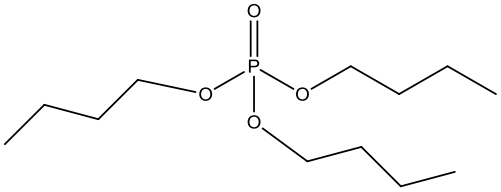
- Recycling part of the spent nuclear fuel
- Uranium and plutonium
- Based on liquid–liquid extraction ion-exchange

Nuclear fuel cycle



NEW EXTRACTIVE MOLECULES REQUIREMENT

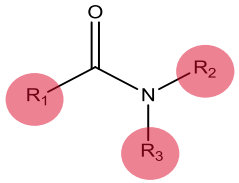
TBP: Historically used



Assets and drawbacks:

- ✓ Highly effective
- ❖ Phosphorous atom
- ❖ Degradation products hardly manageable
- ❖ Redox U/Pu separation

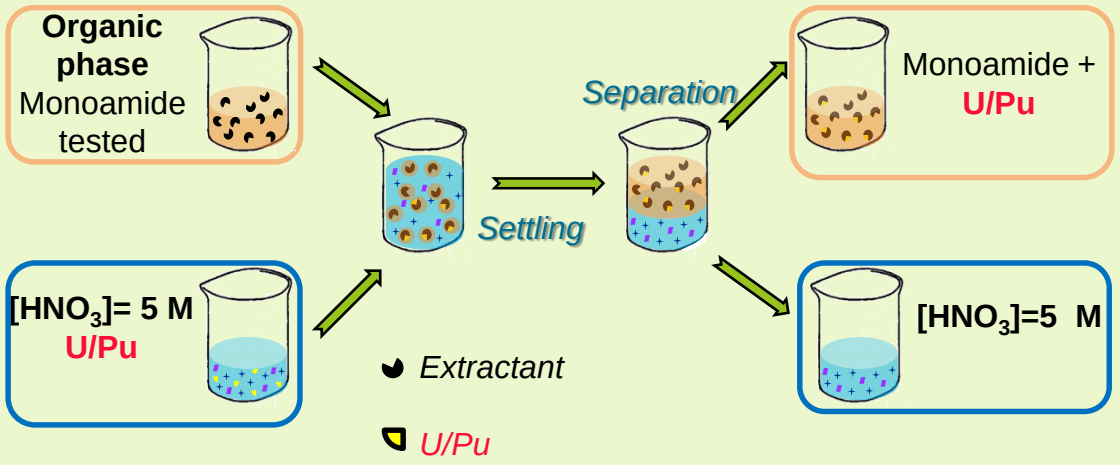
Monoamide: next generation of extractive molecules



Assets and drawbacks:

- ✓ CHON principle respected
- ✓ Incinerable
- ✓ Easy U/Pu separation

Current screening procedure :



Screening procedure of the monoamide is fastidious and costly due to:

- synthesis,
- purification,
- use of radiochemicals

Volume reduction

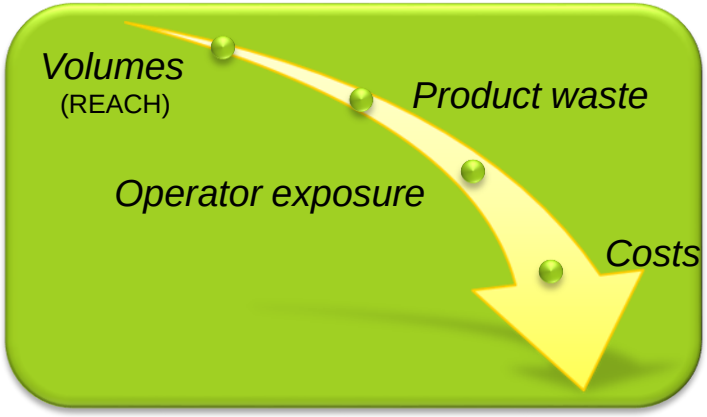
OBJECTIVES

Aim of the study

Conception of a unique screening tool for the monoamides featuring:

- Few manipulations
- Low amount of reagents (radionuclides and extractant)
- Limited generated wastes

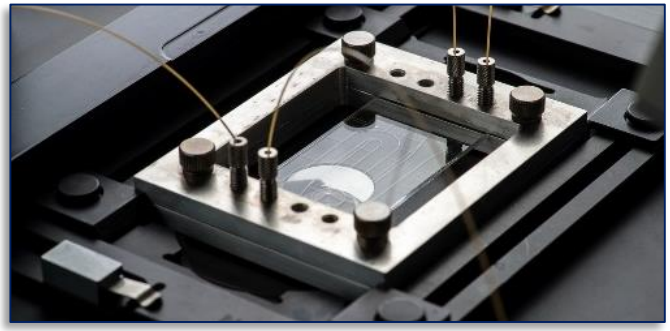
Microfluidics for the screening



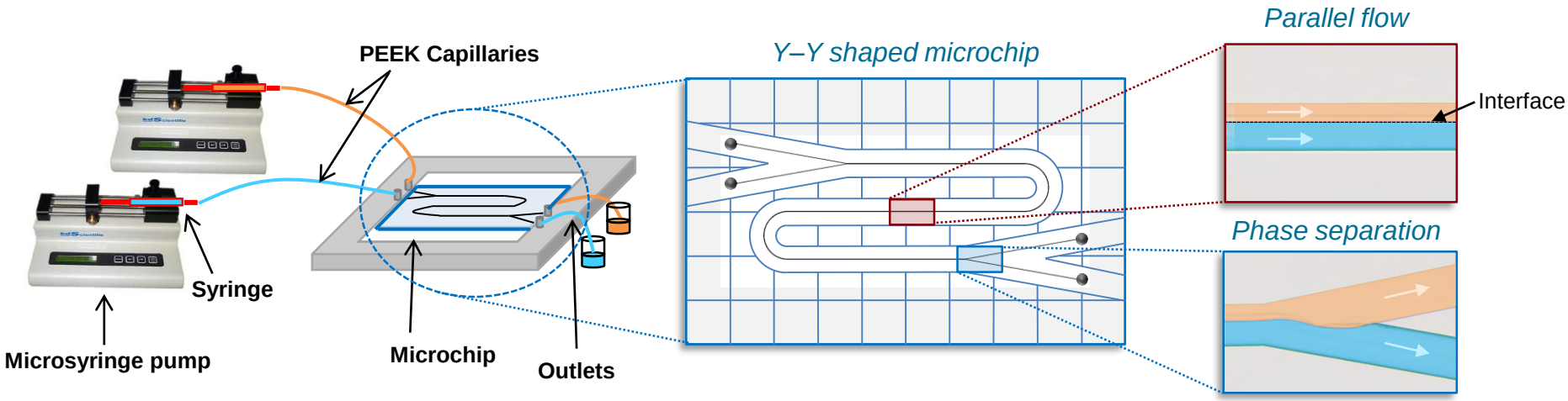
Classic hydrodynamic principles conserved [1]

[1] Whitesides, *Nature*, 2006, 442, 368-373

EXPERIMENTAL SET-UP



- Pyrex glass microchips (IMT, Japan)
  - ✓ Resistance toward corrosive products (concentrated acid, solvents, radionuclides)
- Channel geometry
  - ✓ High interfacial area A' = A/V = 10^4 m^{-1}
    - Height ***H*** = 100 µm
    - Width ***W*** = 40 µm
    - Length ***L*** = 12 cm



Experimental conditions

- **Parallel flows**
- **Centered interface** } Phase separation
- **Suitable contact time** for efficient extraction

$$t_{aq} = \frac{h\,W\,L}{Q_{aq}}$$

HYDRODYNAMICS CONTROL FOR ONE CHEMICAL SYSTEM

Simple case: U-TBP reference chemical system

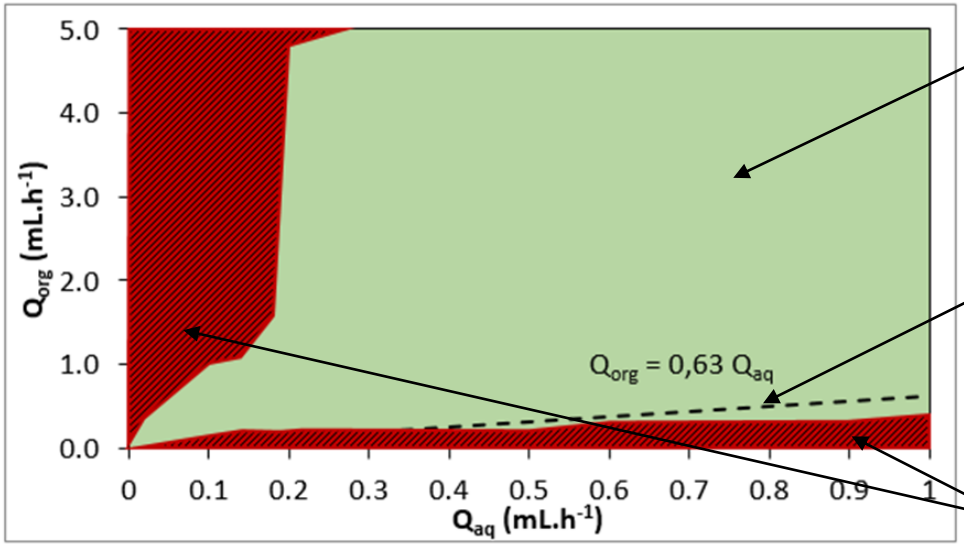
30 % TBP in *n*-dodecane (v/v) / μ_{org} = 1,97 ± 0,01 mPa.s
[U(VI)] = 10^{-4} M in [HNO_3] = 3 M / μ_{aq} = 1,22 ± 0,01 mPa.s

- ❑ **Only one extractant**
- ❑ **Low concentration of uranium**
- ❑ **Viscosities unchanged**

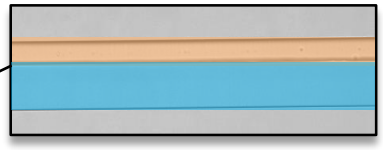
Extraction equilibrium

$$UO_2^{2+} + 2NO_3^- + 2\overline{TBP} \rightarrow \overline{UO_2(NO_3)_2.2TBP}$$

Flow patterns of the biphasic system



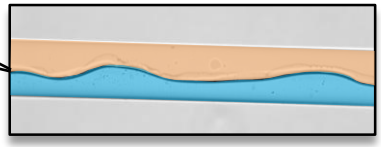
Non-centered interface



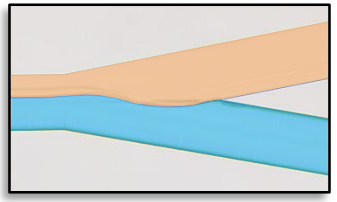
Centered interface



Instable flows



Good separation

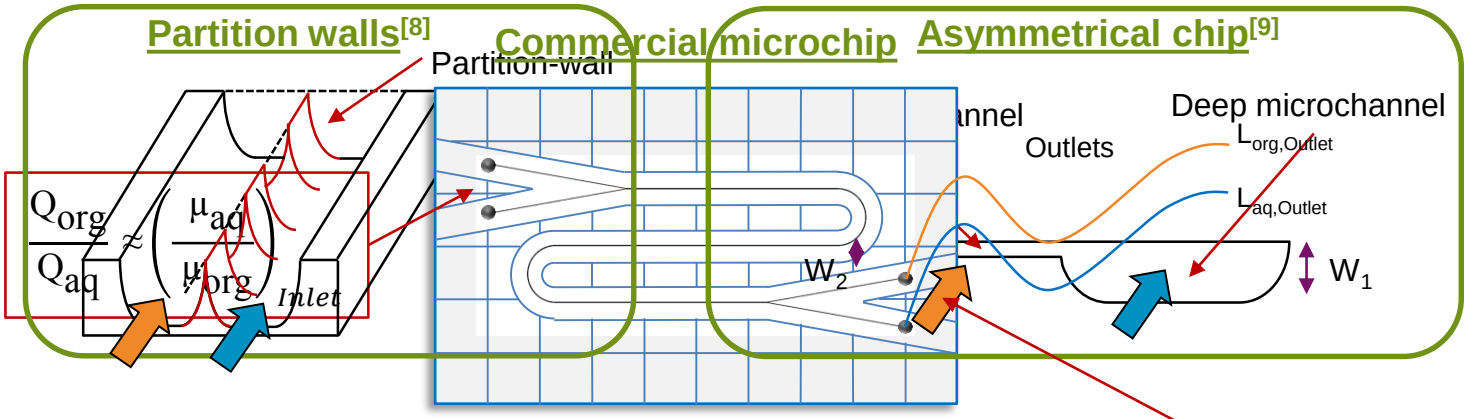


$$\frac{Q_{org}}{Q_{aq}} \approx \frac{\mu_{aq}}{\mu_{org}}$$

SPECIFICITY OF HYDRODYNAMICS CONTROL FOR THE SCREENING OF EXTRACTANTS

More difficult, if:

- **Several extractants with different viscosities**
- the viscosities evolve along the stream because high **concentrations**



Limitations:

- **Challenging conception**
- **Impact on the interfacial area**
- **Specific geometry for one chemical system**

$$\frac{Q_{org}}{Q_{aq}} \approx \left(\frac{\mu_{aq}}{\mu_{org}}\right)_{Outlet} \times \left(\frac{L_{aq}}{L_{org}}\right)_{Outlet}$$

[8] Maruyama et al., Analyst, 2004, 129, 1008-1013
[9] Ban et al., J Nucl Sci Tech, 2011, 48, 1313-1318

Screening tool specifications

Main requirement for the screening tool:

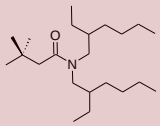
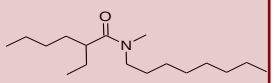
- **Same device** for a wide **range of molecules**
- **Screening with high U and Pu concentrations (≥ 10 g/L)**

Main challenges

- **Each molecule** owns a **specific viscosity**
- The **viscosities evolve** between inlets and the outlets

Conception strategy for the screening tool:

- **Two monoamides** known for their respectively **low** and **high viscosities were used**

Molecule	MOEHA	DEHDMBA
Formula		
Viscosity at 1.4 M in THP (mPa.s)	4.02 ± 0.01	8.04 ± 0.01

Parameters

- **U(VI)** in $[HNO_3]$ = 5 M
- [Monoamide] = 1.4 M in THP

Extraction equilibrium

$$UO_2^{2+} + 2NO_3^- + 2\overline{monoamide} \rightarrow \overline{UO_2(NO_3)_2.2monoamide}$$

Two objectives:

- **Parallel flows and centered interface for any monoamide**
- **Compare the efficiency of the monoamides**

Determination of a common hydrodynamic protocole for monoamides

Inlet stream control

Flow rate ratio Range:

$\frac{Q_{org}}{Q_{aq}}$

Specific Flow rate

$\mu_{org} \Rightarrow Q_{org}$

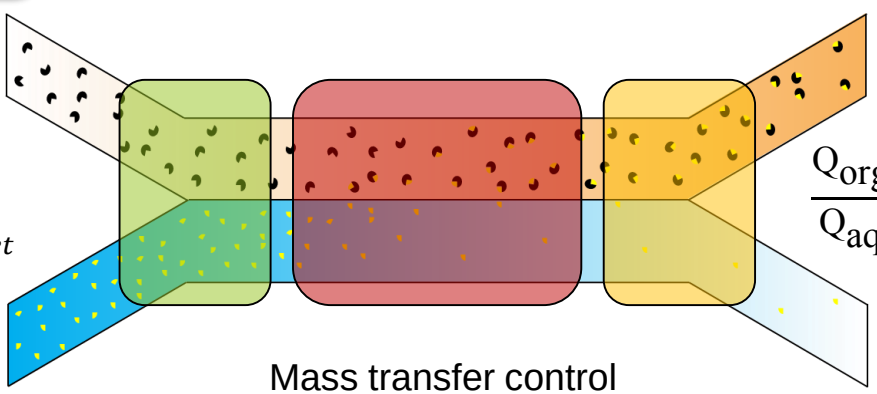
$$\frac{Q_{org}}{Q_{aq}} \approx \left(\frac{\mu_{aq}}{\mu_{org}}\right)_{Inlet}$$

Outlet stream control

Common Length ratio:

$\left(\frac{L_{aq}}{L_{org}}\right)_{Outlet}$

$$\frac{Q_{org}}{Q_{aq}} \approx \left(\frac{\mu_{aq}}{\mu_{org}}\right)_{Outlet} \times \left(\frac{L_{aq}}{L_{org}}\right)_{Outlet}$$



Mass transfer control

Common Contact time:

$t_{aq} = \frac{h\,W\,L}{Q_{aq}}$

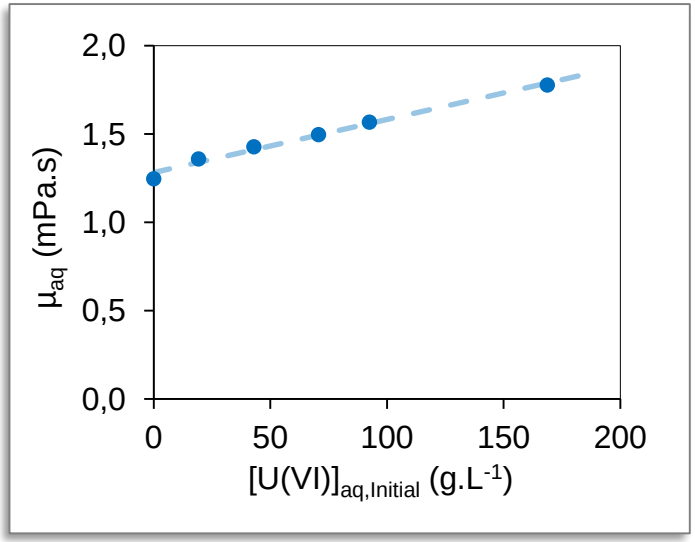
MICROFLUIDIC SCREENING TOOL FOR MONOAMIDES

Flow rate ratio Range:
$\frac{Q_{org}}{Q_{aq}}$

1st step: Determination of the suitable flow rate ratio

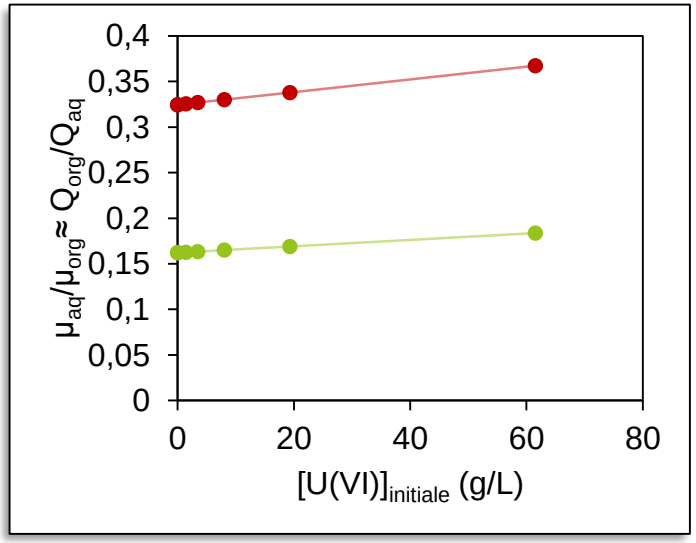
- **With the aqueous and organic phase initial viscosities:**

$$\left(\frac{\mu_{aq}}{\mu_{org}}\right)_{Inlet} \approx \left(\frac{Q_{org}}{Q_{aq}}\right)_{Inlet}$$



Evolution of the aqueous phase viscosity [HNO_3] = 5 M with [U(VI)].

$4.02 \leq \mu_{org} \leq 8.04$ mPa.s



Evolution of the aqueous flow rate ratio for MOEHA and DEHDMBA at 1.4 M with [HNO_3] = 5 M depending on [U(VI)].

Any inlet **flow rate ratio** can be determined knowing the **organic phase viscosity**

MICROFLUIDIC SCREENING TOOL FOR MONOAMIDES

Common Length ratio: $\left(\frac{L_{aq}}{L_{org}}\right)_{Outlet}$

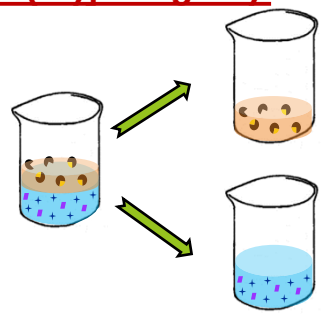
2cd step: Determination of the suitable Outlet length ratio

- **With batch experiments according to:**

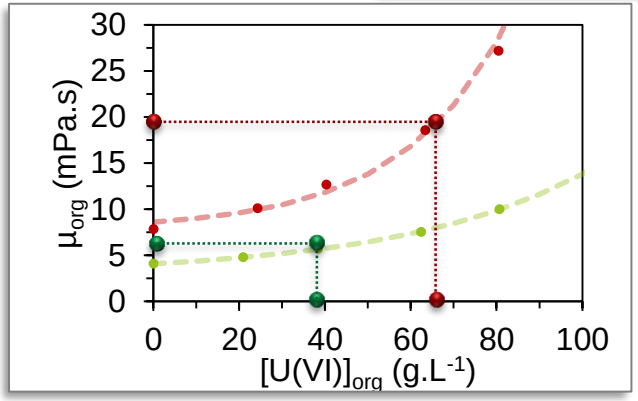
$$\frac{Q_{org}}{Q_{aq}} \approx \left(\frac{\mu_{aq}}{\mu_{org}}\right)_{Outlet} \times \frac{L_{aq}}{L_{org}}$$

Batch experiments ([U(VI)]=20 g.L^{-1})

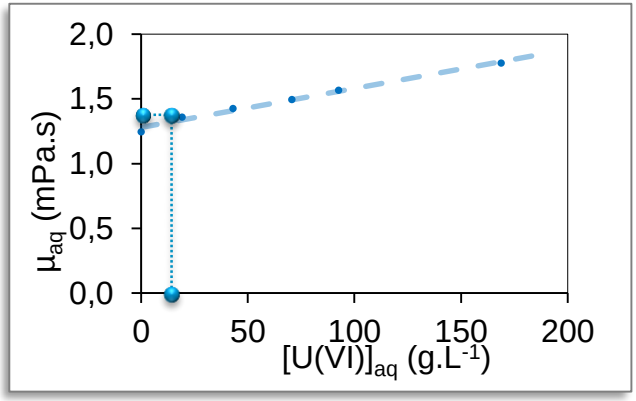
$$\frac{V_{org}}{V_{aq}} = \frac{Q_{org}}{Q_{aq}}$$



Monoamide	MOEHA	DEHDMBA
$\left(\frac{\mu_{aq}}{\mu_{org}}\right)_{Inlet} \approx \frac{Q_{org}}{Q_{aq}}$	0.34	0.17
$\left(\frac{\mu_{aq}}{\mu_{org}}\right)_{Outlet}$	0.20	0.07
$\frac{L_{aq}}{L_{org}}$	2.5	1.7



Evolution of the organic phases viscosities with [U(VI)] in the organic phase after extraction, V_{org}/V_{aq} = 1, T = 293 K. [DEHDMBA] = 1.4 M (red) and [MOEHA] = 1.4 M (green), (diluted in THP)



Evolution of the aqueous phase viscosity [HNO_3] = 5 M with [U(VI)].

The outlet **length ratio** is determined with the **batch extraction yields**

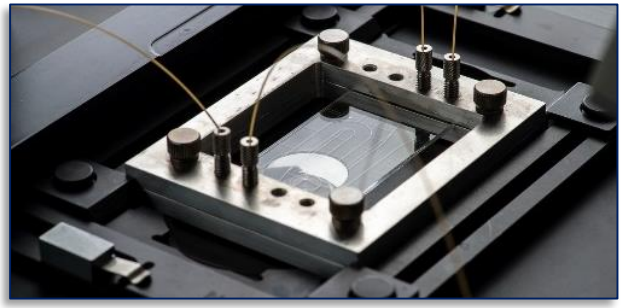
MICROFLUIDIC SCREENING TOOL FOR MONOAMIDES

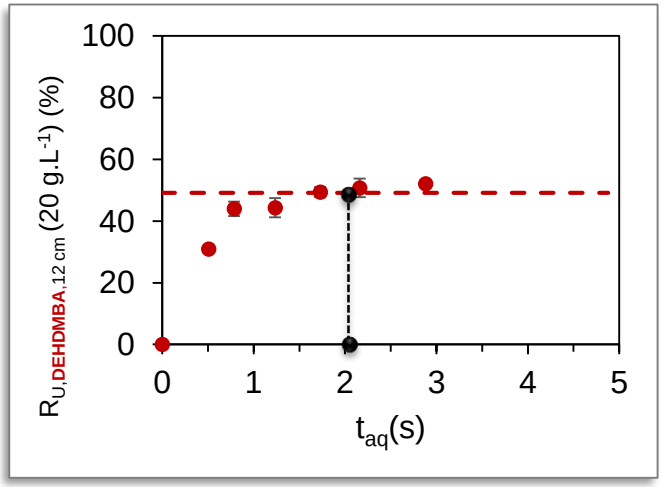
Common Contact time:

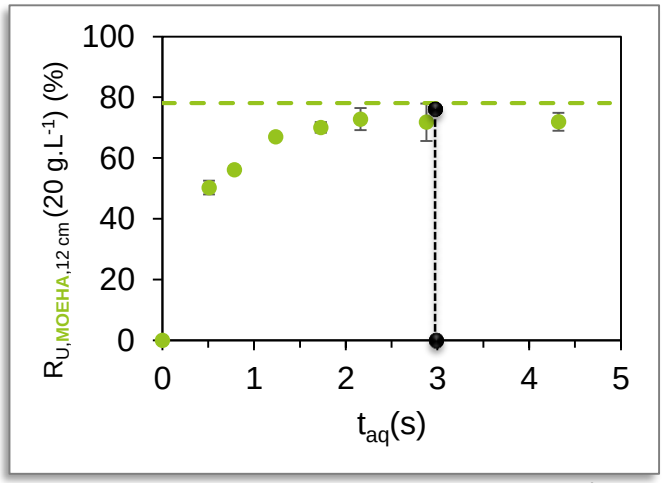
$$t_{aq} = \frac{h\,W\,L}{Q_{aq}}$$

3rd step: Determination of a suitable contact time

- **With solvent extraction experiments in microsystem with:**
  - Chip length: 12 cm
  - Flow rates ratio: **0.17** and **0.34**
  - Outlet length ratio: $L_{aq} = 2 \times L_{org}$







Extraction kinetic profils obtained with [DEHDMBA] = 1.4 M, [MOEHA] = 1.4 M . With ICC-DY15 (12 cm), [U(VI)] =20 g.L^{-1} in [HNO_3] = 5 M and [monoamide] = 1.4 M, and $L_{aq,Outlet}/L_{org,Outlet}$ = 2, T = 293 K.

Equilibrium reached in **3 seconds**
or with a maximum flow rate of **Q_{aq} = 0.3 mL.h^{-1}**

MICROFLUIDIC SCREENING TOOL FOR MONOAMIDES

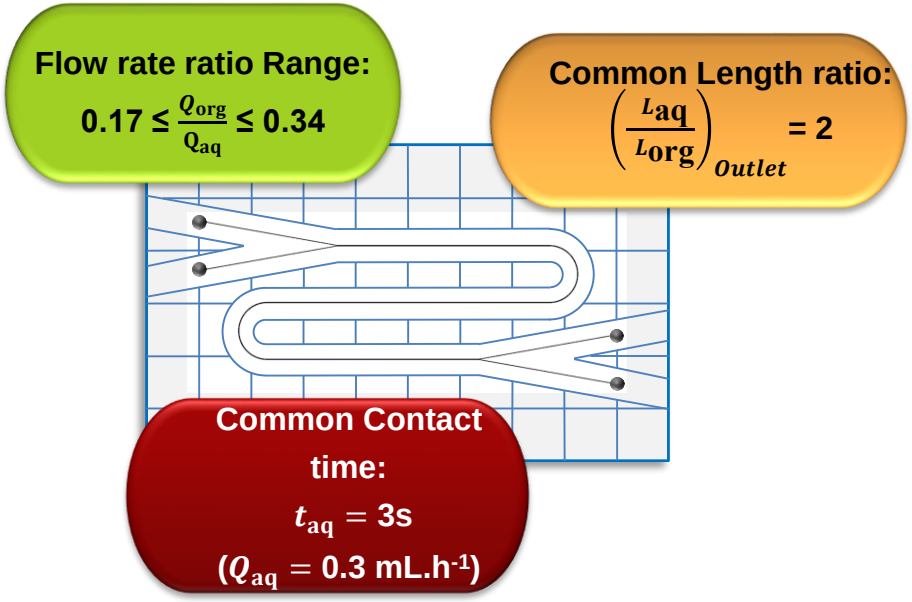
1st Objective: Parallel flows and centered interface for any monoamide

Initial parameters

- **U(VI)** in $[HNO_3]$ = 5 M
- [Monoamide] = 1.4 M in THP

Hydrodynamic parameters

- Chip length: **12 cm**
- Flow rates ratio: **0.17** and **0.34**
- Outlet length ratio: $L_{aq} = 2 \times L_{org}$
- Aqueous flow rate: $Q_{aq} = 0.3\ mL.h^{-1}$



2cd Objective: Compare the efficiency of the monoamides

Specific viscosity → μ_{org} → Specific Flow rate → Q_{org} → Normalized Yield

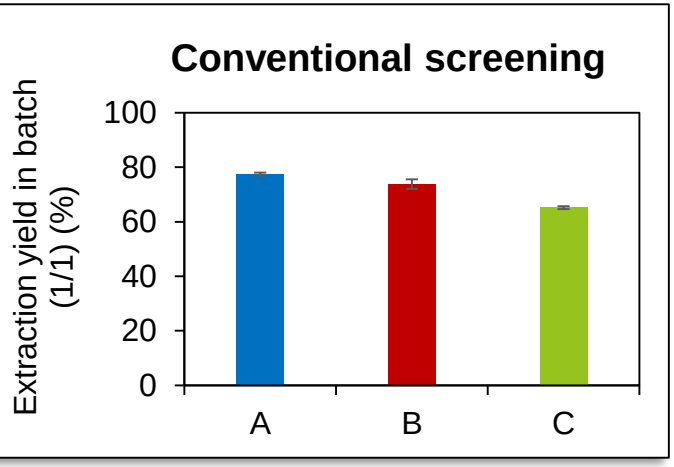
$$R_N = \frac{R_{Chip}}{100 \times \frac{Q_{org}}{Q_{aq}}}$$

MICROFLUIDIC SCREENING TOOL FOR MONOAMIDES

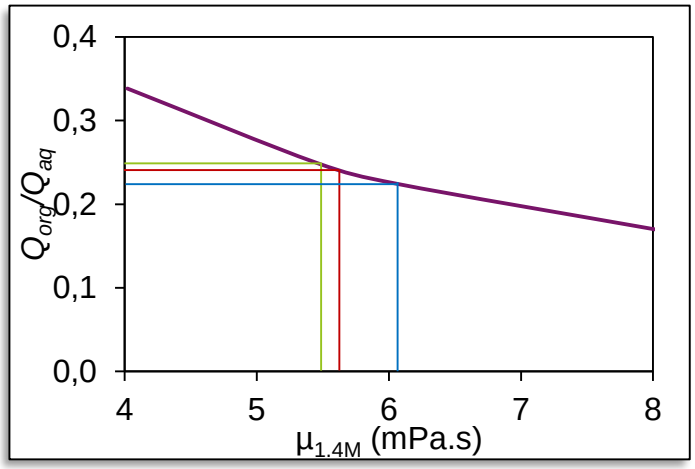
Validation of the method for [U(VI)] =20 g.L^{-1}

Screening of 3 monoamides A, B, C

Monoamide	A	B	C
Viscosity at 1.4 M in THP (mPa.s)	6.07	5.6	5.45

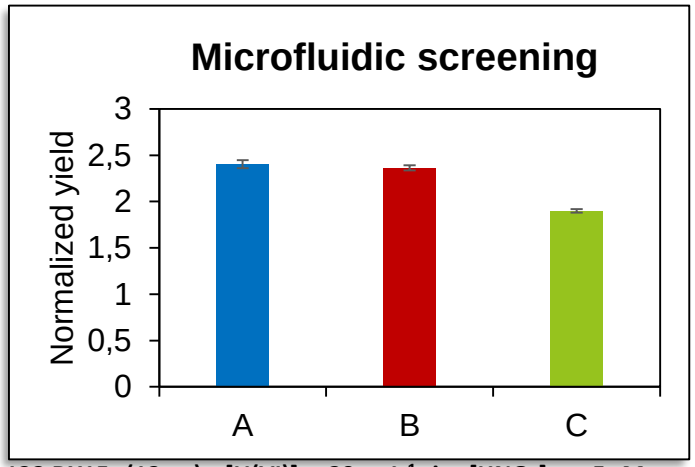


ICC-DY15 (12cm), [U(VI)] =20 g.L^{-1} in [HNO_3] = 5 M and [monoamide] = 1.4 M, and V_{aq}/V_{org}= 1, T = 293 K.



flow rate ratio evolution depending on the viscosity of the organic phase containing monoamide diluted 1.4 M in THP with $[U(VI)]_{Initial}$ = 20 g.L^{-1}

$$R_N = \frac{R_{Chip}}{100 \times \frac{Q_{org}}{Q_{aq}}}$$

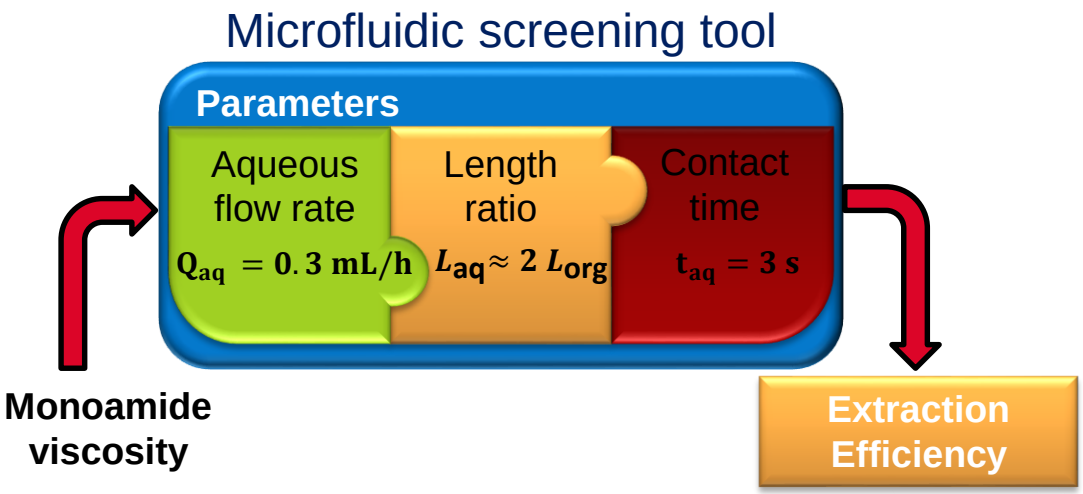


ICC-DY15 (12cm), [U(VI)] =20 g.L^{-1} in [HNO_3] = 5 M and [monoamide] = 1.4 M, and $L_{aq,Outlet}/L_{org,Outlet}$ = 2, T = 293 K.

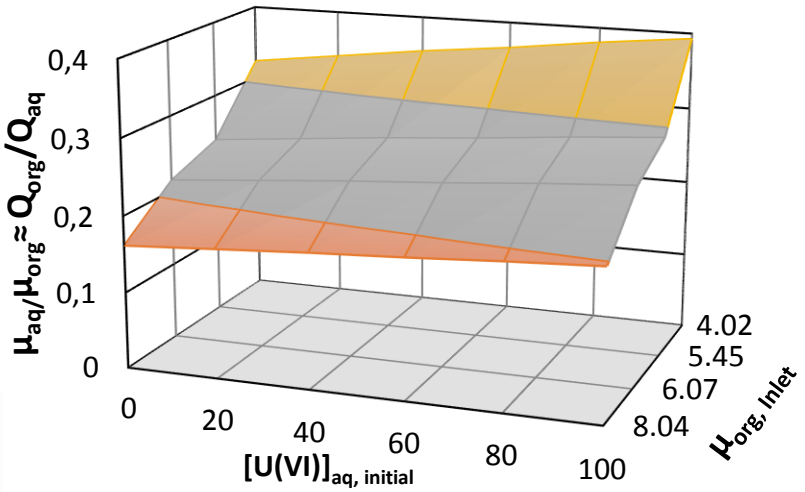
Same relative **performances** as batch experiments

CONCLUSION AND PERSPECTIVES

Conclusion



Establishment of a viscosity/phase ratio diagram



flow rate ratio evolution depending on the viscosity of the organic phase containing monoamide diluted 1.4 M in THP and $[U(VI)]_{Initial}$ in aqueous phase.

- ✓ Only 20 µL of solution are need
- ✓ Screening method can be applicable with large range of uranium concentration
- ✓ This conception strategy applicable on other kind of molecules

Perspectives

- ✓ CFD simulation (COMSOL) for the design of a custom-made chip
  - Asymetrical geometry
  - More suitable length of microchip
  - Test with U(VI) and Pu(IV)



Publication

J.P. Jasmin and al. *Solvent Extraction of Concentrated Uranium (VI) by 30 % TBP in a Parallel Flows Microsystem: Towards a Tool for Screening New Extractant Molecules*
Solvent Extraction and Ion Exchange**, 2017,vol 35**
http://dx.doi.org/10.1080/07366299.2017.1308151

Patent

Patent pending work:
BD17584 (application submitted on december 2016)