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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

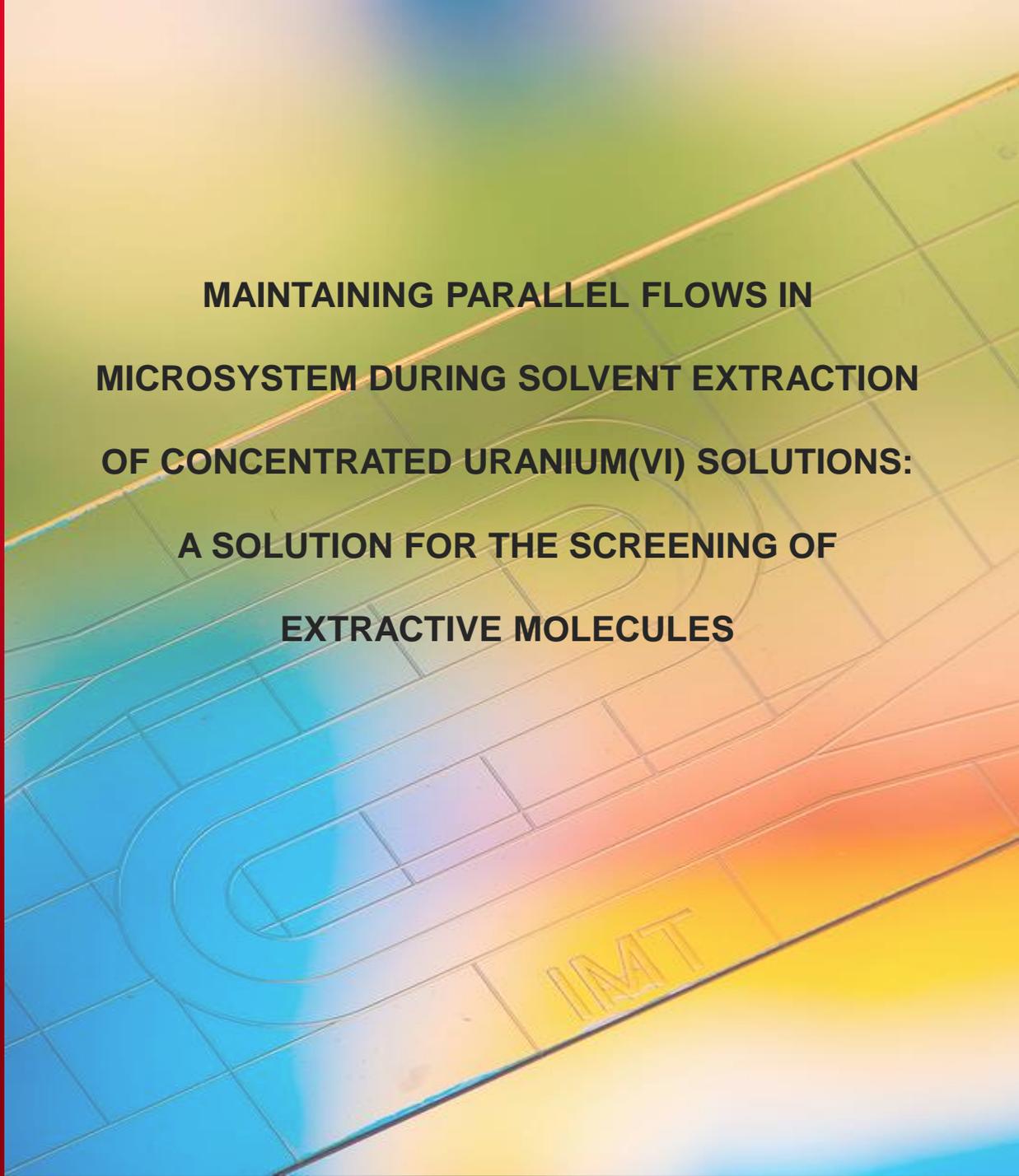


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The background of the right side of the slide is a photograph of a microsystem chip. The chip is a square piece of material with a grid of small rectangular cells. A large, U-shaped channel is visible in the center. The text 'IMAT' is printed on the chip in the lower right quadrant. The background has a color gradient from blue to yellow.

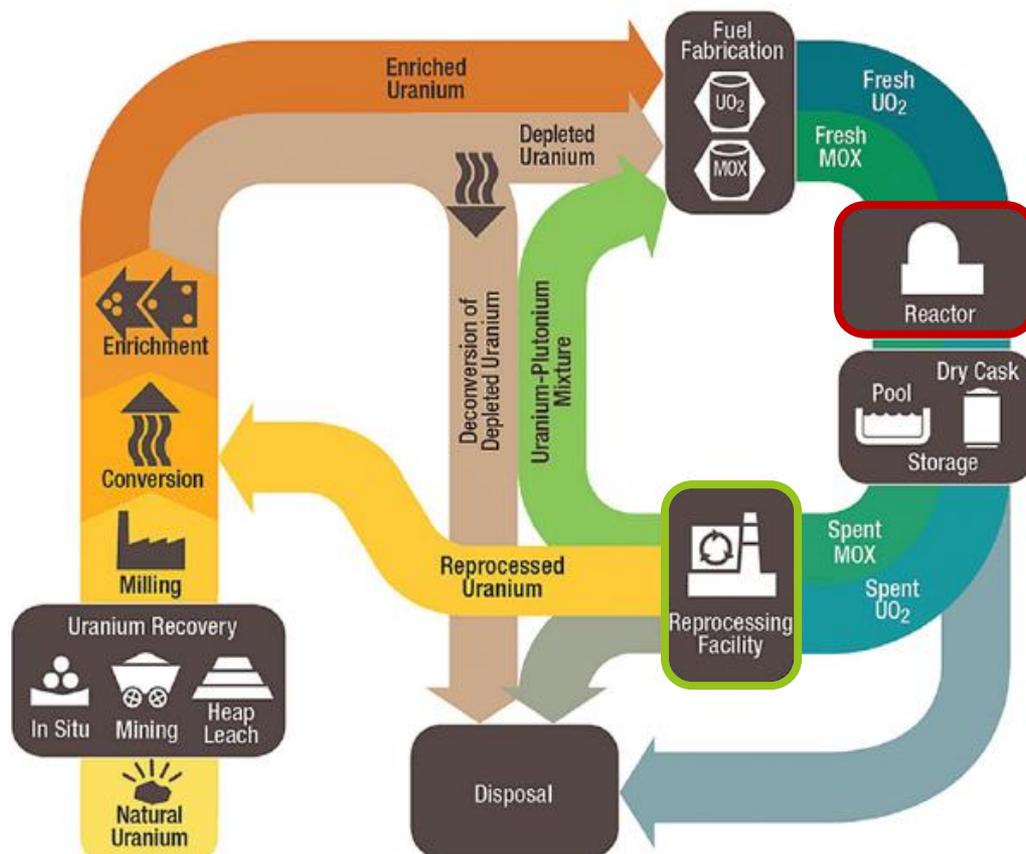
**MAINTAINING PARALLEL FLOWS IN
MICROSYSTEM DURING SOLVENT EXTRACTION
OF CONCENTRATED URANIUM(VI) SOLUTIONS:
A SOLUTION FOR THE SCREENING OF
EXTRACTIVE MOLECULES**

PUREX: Plutonium and Uranium Recovery Extraction

Nuclear plant purpose

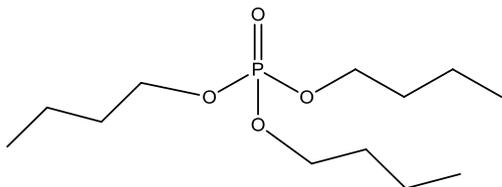
- ❑ Recycling part of the spent nuclear fuel
- ❑ Uranium and plutonium
- ❑ Based on liquid-liquid extraction ion-exchange

Nuclear fuel cycle



NEW EXTRACTIVE MOLECULES REQUIREMENT

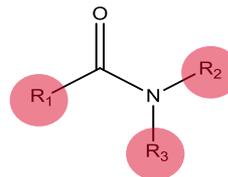
TBP: Historically used



Assets and drawbacks:

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

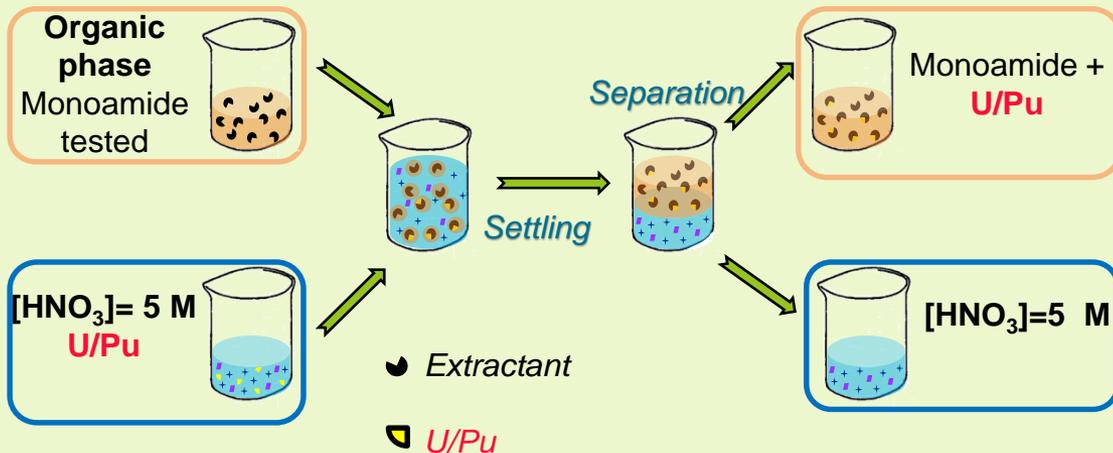
Monoamide: next generation of extractive molecules



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

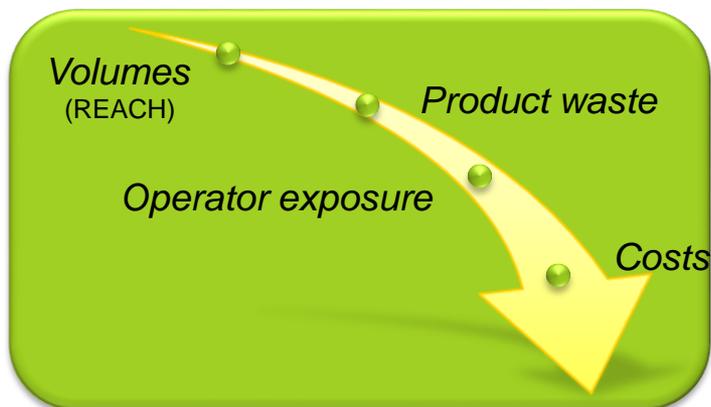
Volume reduction

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

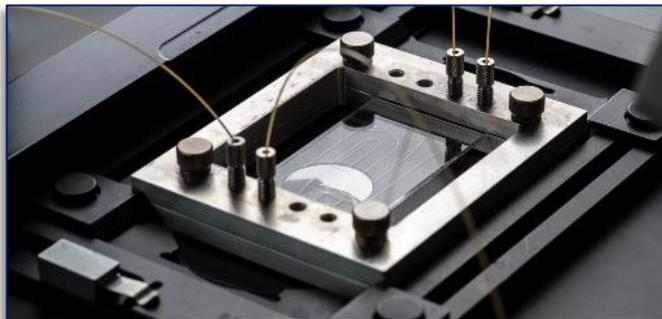
Microfluidics for the screening



Classic hydrodynamic principles conserved [1]

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

EXPERIMENTAL SET-UP



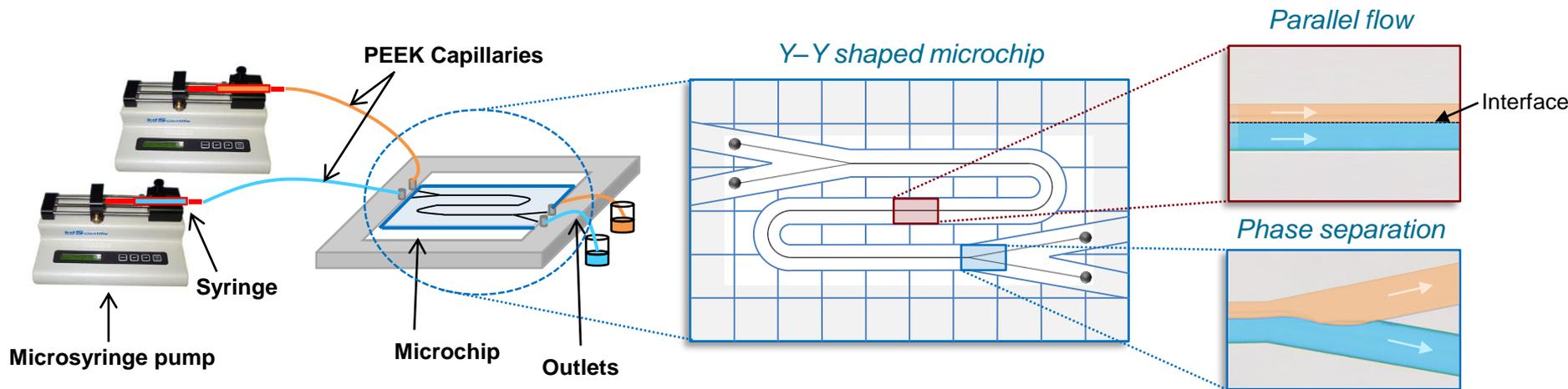
- Pyrex glass microchips (IMT, Japan)

- ✓ Resistance toward corrosive products (concentrated acid, solvents, radionuclides)

- Channel geometry

- ✓ High interfacial area
 $A' = A/V = 10^4 \text{ m}^{-1}$

$$\left\{ \begin{array}{l} \text{Height } H = 100 \mu\text{m} \\ \text{Width } W = 40 \mu\text{m} \\ \text{Length } L = 12 \text{ cm} \end{array} \right.$$



Experimental conditions

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

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

Simple case: U-TBP reference chemical system

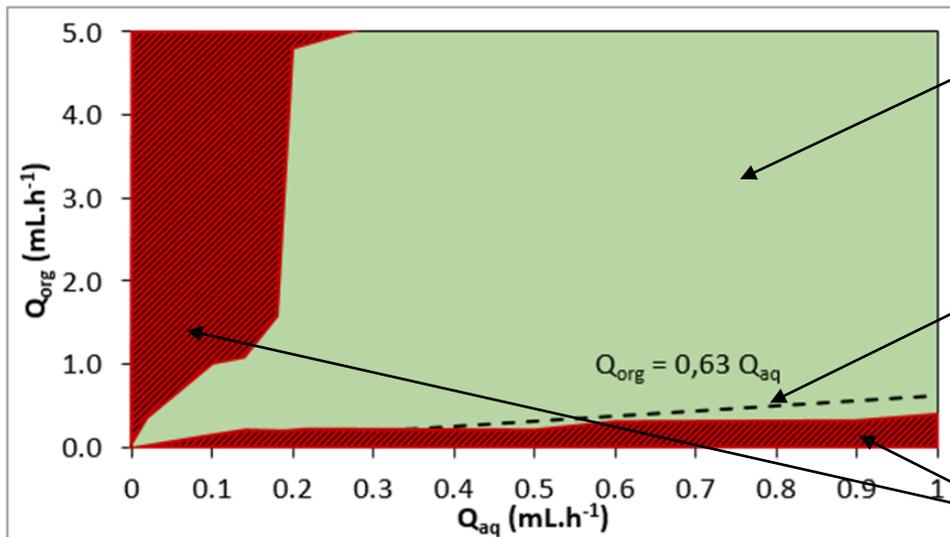
$$\left\{ \begin{array}{l} 30\% \text{ TBP in } n\text{-dodecane (v/v)} / \mu_{\text{org}} = 1,97 \pm 0,01 \text{ mPa.s} \\ [\text{U(VI)}] = 10^{-4} \text{ M in } [\text{HNO}_3] = 3 \text{ M} / \mu_{\text{aq}} = 1,22 \pm 0,01 \text{ mPa.s} \end{array} \right\}$$

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

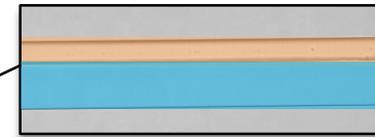
Extraction equilibrium



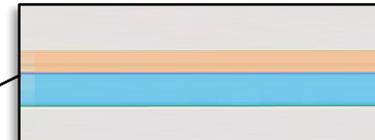
Flow patterns of the biphasic system



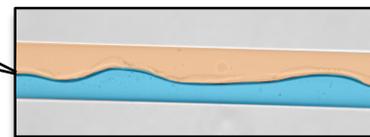
Non-centered interface



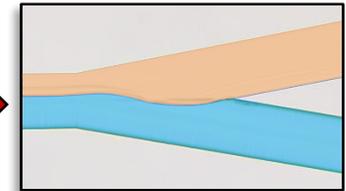
Centered interface



Instable flows



Good separation

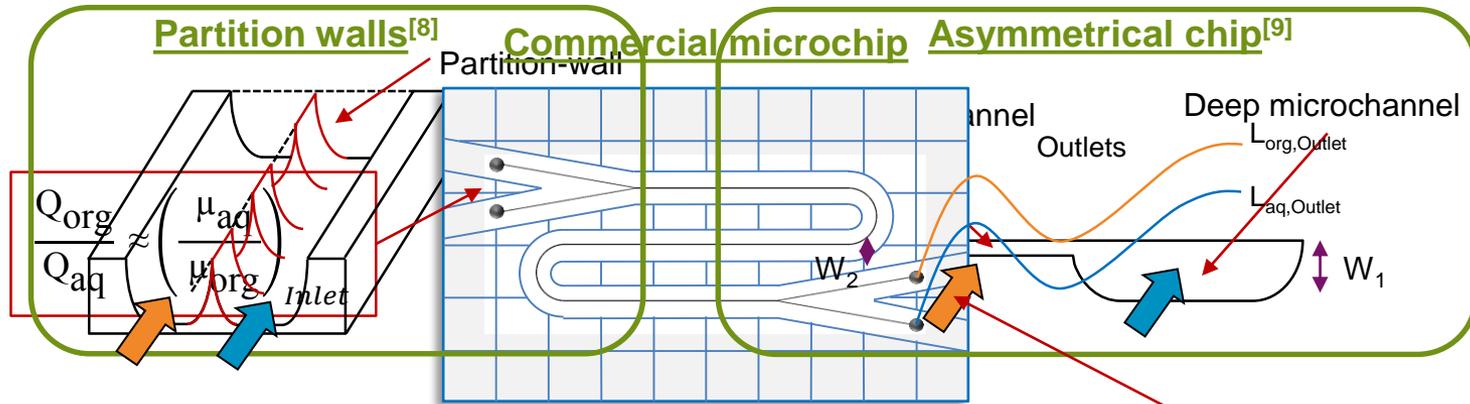


$$\frac{Q_{\text{org}}}{Q_{\text{aq}}} \approx \frac{\mu_{\text{aq}}}{\mu_{\text{org}}}$$

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

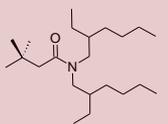
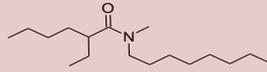
Screening tool specifications

Main requirement for the screening tool:

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

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

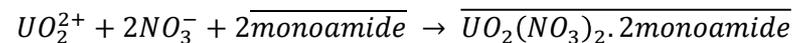
Main challenges

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

Parameters

- U(VI) in $[\text{HNO}_3] = 5$ M
- $[\text{Monoamide}] = 1.4$ M in THP

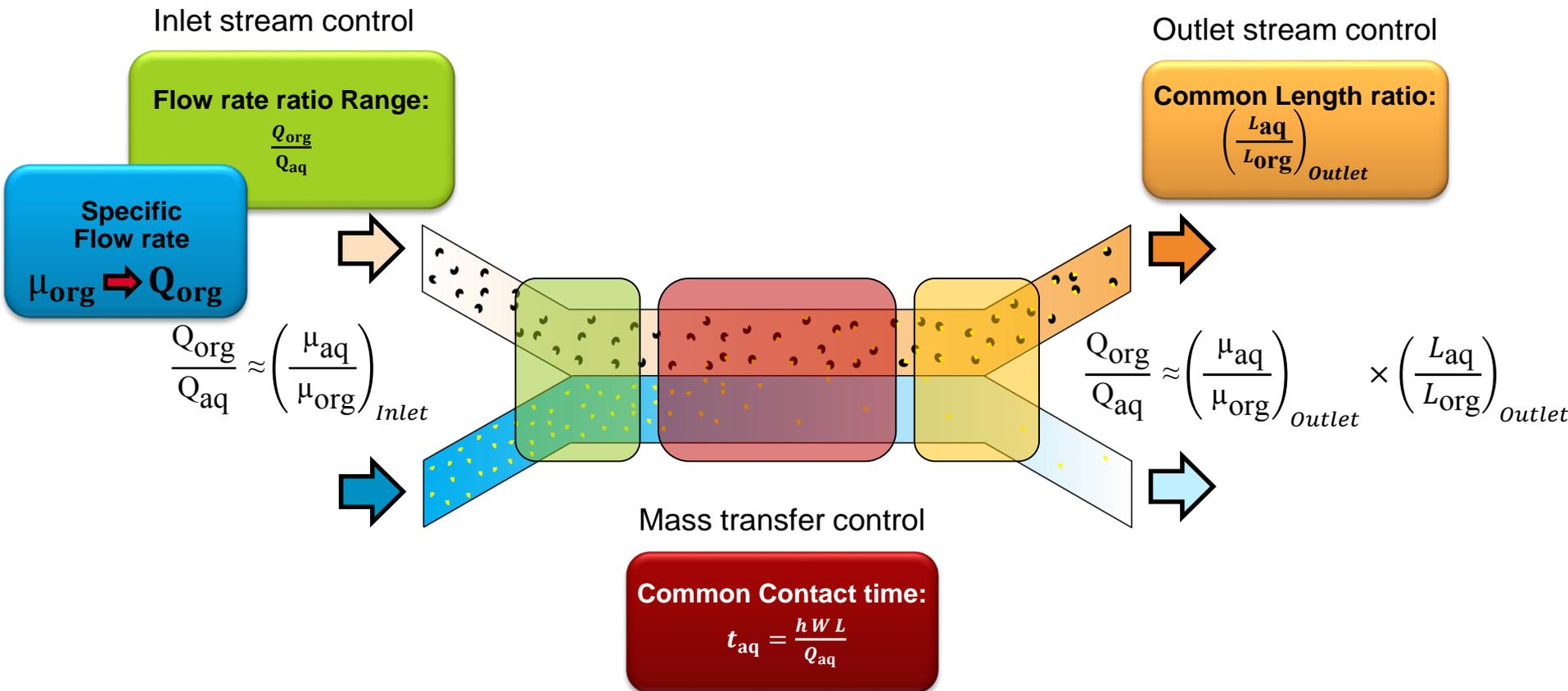
Extraction equilibrium



Two objectives:

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

Determination of a common hydrodynamic protocole for monoamides



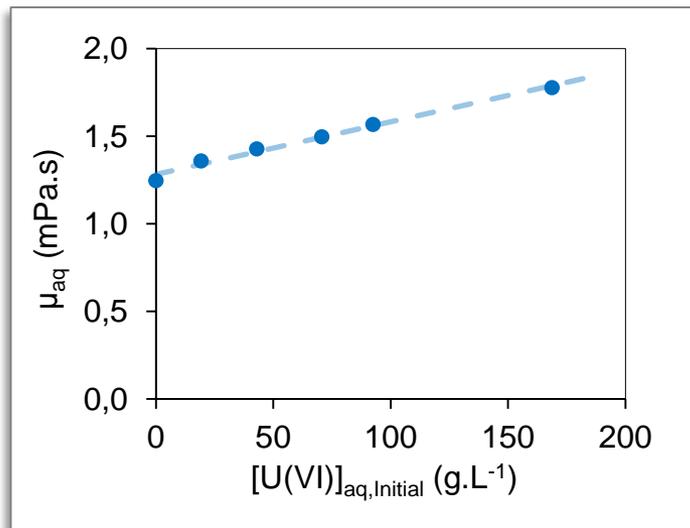
Flow rate ratio Range:

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

1st step: Determination of the suitable flow rate ratio

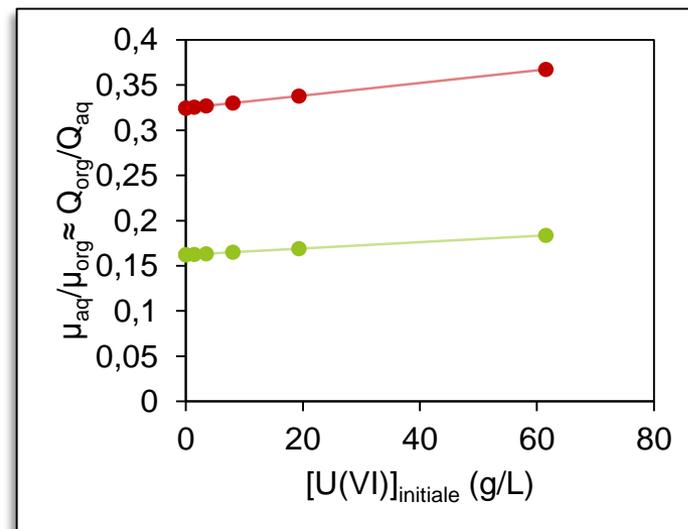
- With the aqueous and organic phase initial viscosities:

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



Evolution of the aqueous phase viscosity [HNO₃] = 5 M with [U(VI)].

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



Evolution of the aqueous flow rate ratio for MOEHA and DEHDMBA at 1.4 M with [HNO₃] = 5 M depending on [U(VI)].

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

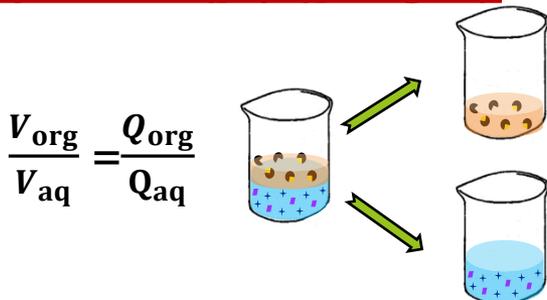
MICROFLUIDIC SCREENING TOOL FOR MONOAMIDES

2^{cd} 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)

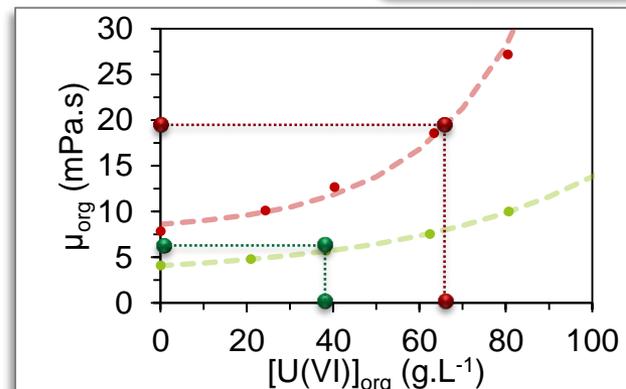


$$\frac{V_{org}}{V_{aq}} = \frac{Q_{org}}{Q_{aq}}$$

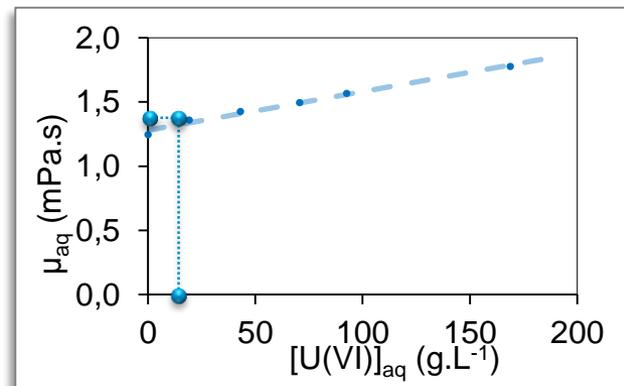
Monoamide	MOEHA	DEHDMBA
$\left(\frac{\mu_{aq}}{\mu_{org}} \right)_{Inlet} \approx \frac{Q_{org}}{Q_{aq}}$	0.34	0.17
$\left(\frac{\mu_{aq}}{\mu_{org}} \right)_{Outlet}$	0.20	0.07
$\frac{L_{aq}}{L_{org}}$	2.5	1.7

Common Length ratio:

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



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 [HNO₃] = 5 M with [U(VI)].

The outlet length ratio is determined with the batch extraction yields

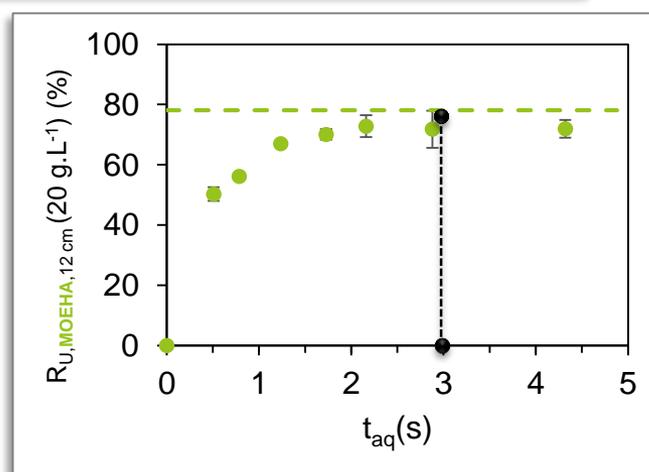
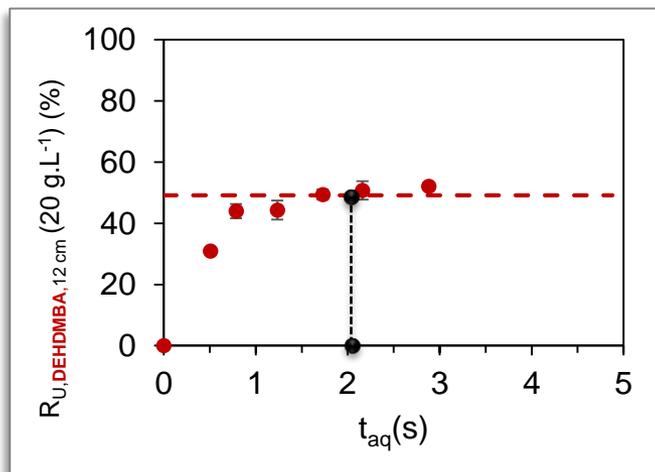
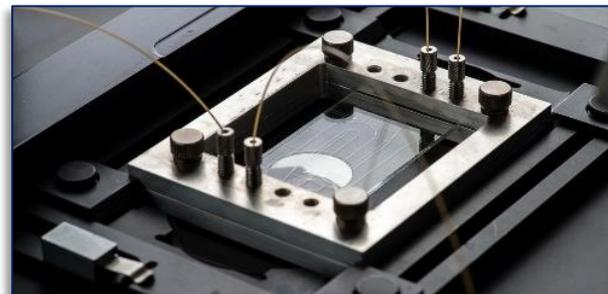
Common Contact time:

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

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 profiles obtained with [DEHD MBA] = 1.4 M, [MOEHA] = 1.4 M. With ICC-DY15 (12 cm), [U(VI)] = 20 g.L⁻¹ in [HNO₃] = 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 $Q_{aq} = 0.3 \text{ mL.h}^{-1}$

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

- ❑ **U(VI)** in $[\text{HNO}_3] = 5 \text{ M}$
- ❑ $[\text{Monoamide}] = 1.4 \text{ M}$ in THP

Hydrodynamic parameters

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

Flow rate ratio Range:

$$0.17 \leq \frac{Q_{\text{org}}}{Q_{\text{aq}}} \leq 0.34$$

Common Length ratio:

$$\left(\frac{L_{\text{aq}}}{L_{\text{org}}} \right)_{\text{Outlet}} = 2$$

Common Contact
time:

$$t_{\text{aq}} = 3\text{s}$$

$$(Q_{\text{aq}} = 0.3 \text{ mL.h}^{-1})$$

2^{cd} Objective: Compare the efficiency of the monoamides

Specific viscosity

 μ_{org} 

Specific Flow rate

 Q_{org} **Normalized Yield**

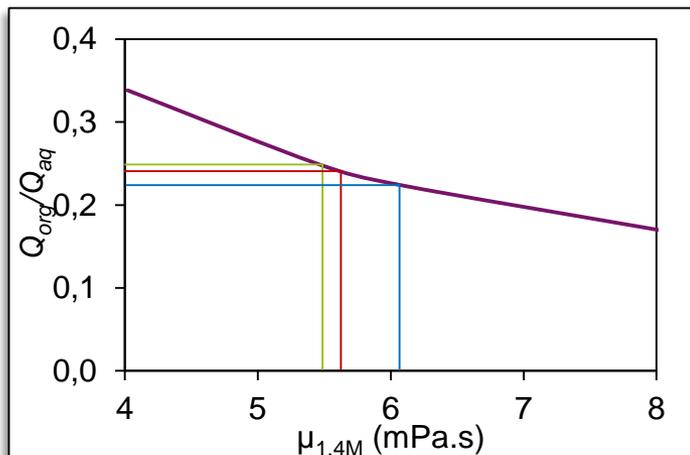
$$R_N = \frac{R_{\text{chip}}}{100 \times \frac{Q_{\text{org}}}{Q_{\text{aq}}}}$$

MICROFLUIDIC SCREENING TOOL FOR MONOAMIDES

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

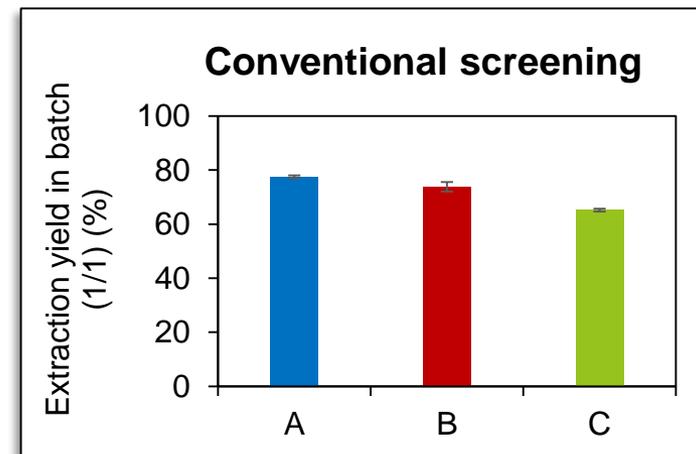
Screening of 3 monoamides A, B, C

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

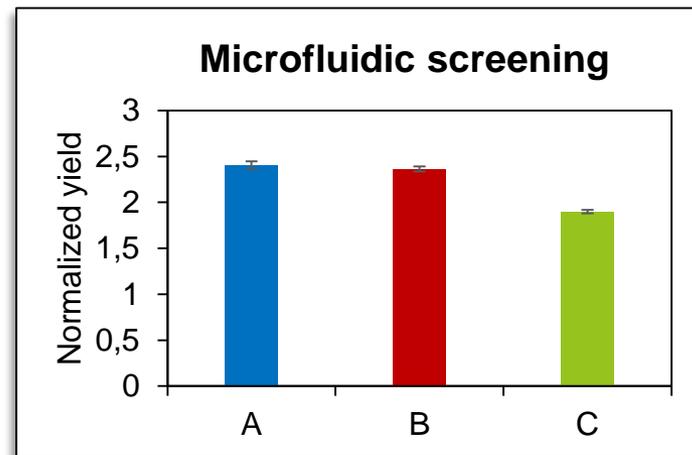


flow rate ratio evolution depending on the viscosity of the organic phase containing monoamide diluted 1.4 M in THP with $[U(VI)]_{\text{initial}} = 20 \text{ g.L}^{-1}$

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



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



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

Same relative performances as batch experiments

Conclusion

Microfluidic screening tool

Parameters

Aqueous flow rate

$$Q_{aq} = 0.3 \text{ mL/h}$$

Length ratio

$$L_{aq} \approx 2 L_{org}$$

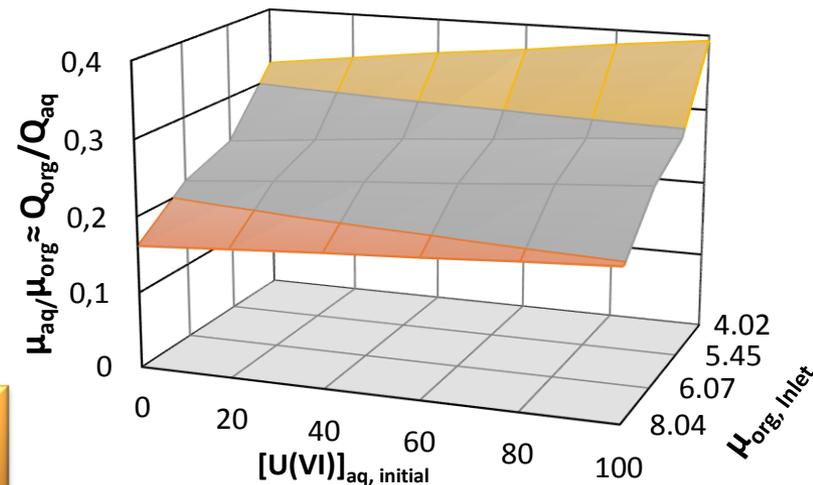
Contact time

$$t_{aq} = 3 \text{ s}$$

Monoamide viscosity

Extraction Efficiency

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
 - Asymmetrical geometry
 - More suitable length of microchip
 - Test with U(VI) and Pu(IV)



Thank your
Attention

Question?

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)