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Liquid-liquid extraction of two radiochemical systems at micro-scale predict and achieve segmented flow to optimize mass transfer

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DE LA RECHERCHE À L'INDUSTRIE



Axel Vansteene, J.P. Jasmin, René Brennetot, Clarisse Mariet¹

¹ Den – Service d'Etudes Analytiques et de Réactivité des Surfaces (SEARS), CEA, Université Paris-Saclay, F-91191, Gif sur Yvette, France

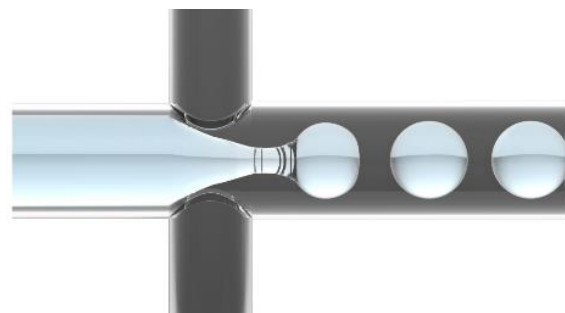
Siméon Cavadias, Gérard Cote²

² PSL Research University, Chimie ParisTech - CNRS, Institut de Recherche de Chimie Paris, 75005, Paris, France



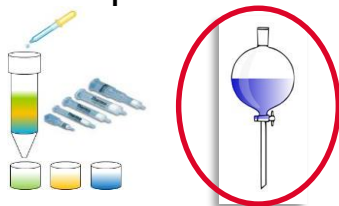
PhD thesis started in November, 2015

«LIQUID-LIQUID EXTRACTION OF TWO RADIOCHEMICAL SYSTEMS AT MICRO-SCALE: PREDICT AND ACHIEVE SEGMENTED FLOW TO OPTIMIZE MASS TRANSFER»



Current nuclear procedures :

- Separation and purification is needed before detection

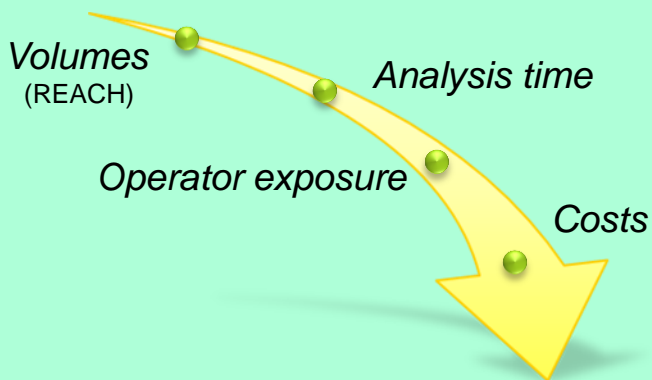


- Hardly implementable in glove boxes
- Huge volumes of solvents

- Radiochemical issues
- Waste (solvents, extractants)

↓ A solution: process intensification

Microfluidics: Manipulate fluids at micro-scale i.e. one dimension of the analytical device is below 100 μm [1]

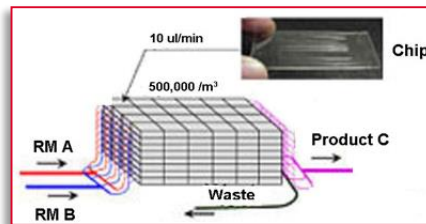


Classical fluid dynamics

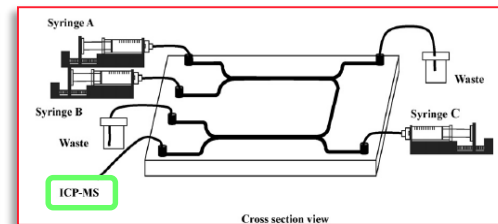
[1] Whitesides, *Nature*, 2006, 442, 368-373

Assets

- Analysis automation and parallelization
- Possible coupling with detection devices



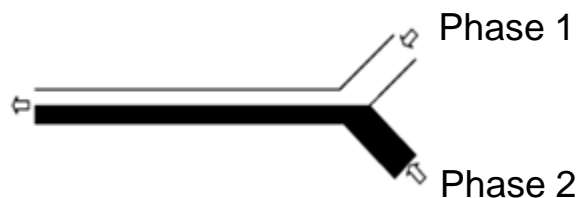
Ralston, ISEC Conference, 2011



Kagawa, Talanta, 2009, 79, 1001

Two types of biphasic flows

Parallel flows (stratified flows)

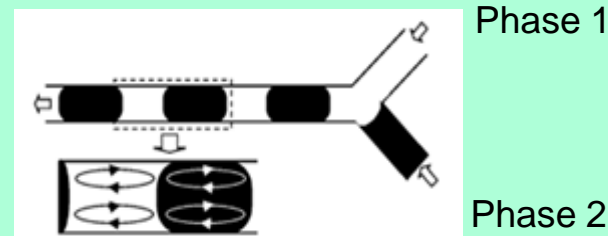


✓ Easy retrieval of the two phases

- ❖ Diffusion-limited
- ❖ Set specific interfacial area (depending on the chip)

Non-suitable for slow kinetics systems

Segmented flow



- ✓ Convection
- ✓ Adjustable specific interfacial area

- ❖ Phase separation to be performed

Suitable for all chemical systems

Comparizon of 2 chemical systems in the same microchip

U(VI) / Aliquat® 336

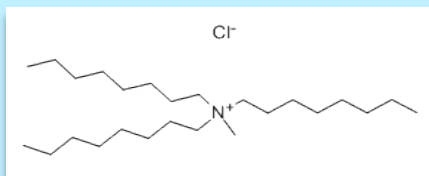
Quick kinetics [2]

Aqueous phase:

[U(VI)] = 10^{-5} M
[HCl] = 5 M

Organic phase :

[Aliquat® 336] = 10^{-2} M in
n-dodécane/ 1-décanol 1% (v/v)



$R_{U, \text{batch, optimal}} = (85.2 \pm 1.2) \% \text{ for } V_{\text{aq}} = V_{\text{org}}$

Viscosity ratio

$\mu_{\text{org}} / \mu_{\text{aq}} \approx 1.2$

Eu(III) / DMDBTDMA

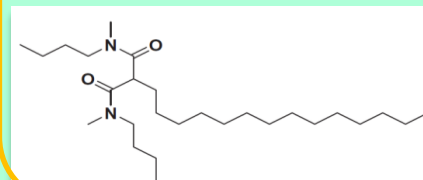
Slow kinetics [3]

Aqueous phase :

[Eu(III)] = 10^{-2} M
[HNO₃] = 4 M

Organic phase :

[DMDBTDMA] = 1 M
n-dodécane



$R_{Eu, \text{batch, optimal}} = (90.1 \pm 0.3) \% \text{ for } V_{\text{aq}} = V_{\text{org}}$

Viscosity ratio

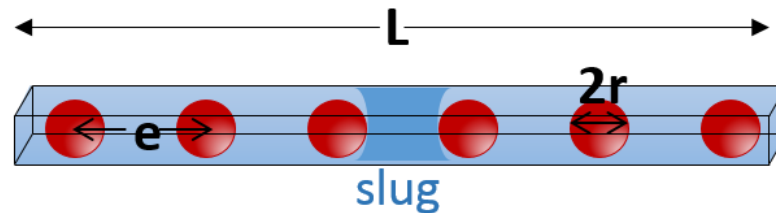
$\mu_{\text{org}} / \mu_{\text{aq}} \approx 14$

[2] Coleman et al., AIME Annual Meeting, 1979, New Orleans, LA, USA

[3] Weigl et al., Solv. Ext. Ion Exch., 2001, 19, 215-229

Will only be presented the Eu(III) / DMDBTDMA chemical system

- Optimize the specific interfacial area $(A/V) = \frac{\text{Interfacial area}}{\text{Microchannel volume}}$
- Determine the segmented flow (i.e. droplets population) characteristics, in order to figure out the specific interfacial area



- ❑ Droplets volume : $V_{plot} = f(\text{physicochemistry, hydrodynamics, chip geometry})$
- ❑ Droplets frequency $f = \frac{Q_d}{V_{plot}}$
- ❑ Spacing between consecutive droplets $e = \frac{Q_c + Q_d}{hw_0 f}$

Physicochemistry

η_i, σ




Hydrodynamics

Q_i

Chip geometry

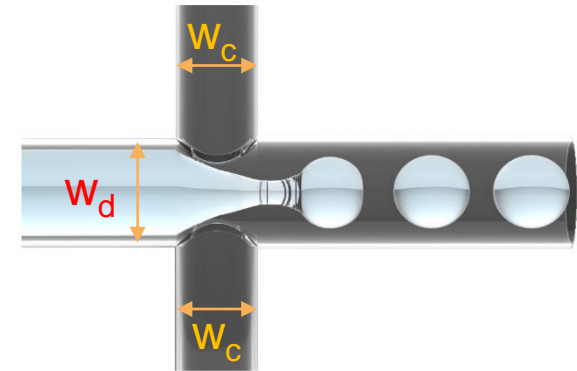
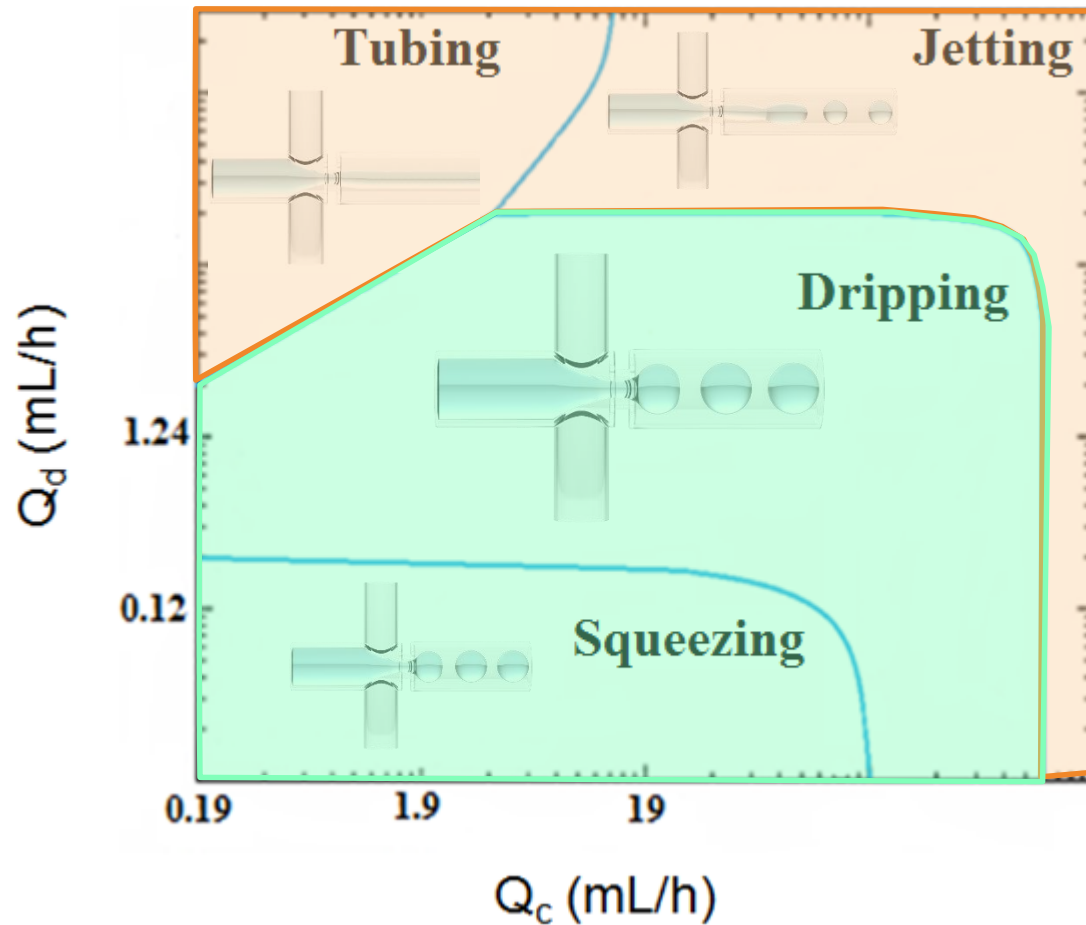
Junction type (T, FF), dimensions

Which junction best suits our needs?

 <p>T-Junction</p>	<ul style="list-style-type: none"> <input type="checkbox"/> Available equations for every flow regime <input type="checkbox"/> Squeezing, transition regime, and dripping regimes to be studied
 <p>Focalized Flux (FF)</p>	<ul style="list-style-type: none"> <input type="checkbox"/> Available equations for every flow regime <input type="checkbox"/> Squeezing, transition regime, and dripping regimes to be studied
 <p>Co-current Flux</p>	<ul style="list-style-type: none"> <input type="checkbox"/> Very few models in the litterature

► Flow regimes to be chosen

FLOW CARTOGRAPHY – FF JUNCTION



$$w_d = w_{or} = w_c = H$$

- ❖ Squeezing
- ❖ Dripping



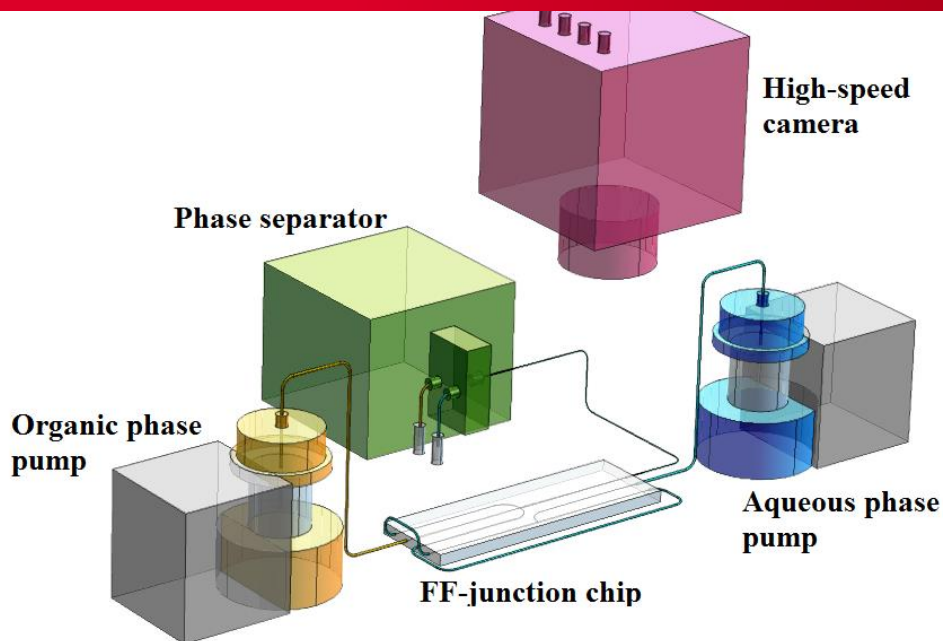
Available equations :

- ❖ Liu and Zhang model [4]
- ❖ Cubaud and Mason model [5]

[4] Liu et al., Physics of Fluids, 2011, 23, 8

[5] Cubaud et al., Physics of Fluids, 2008, 20, 5

EXPERIMENTAL SET-UP



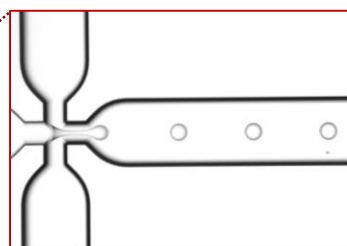
- Glass chip (Dolomite, UK)
- ✓ Corrosive chemicals (Acids, solvents)

Continuous aqueous phase
[Eu(III)] = 10^{-2} M
[HNO₃] = 4 M

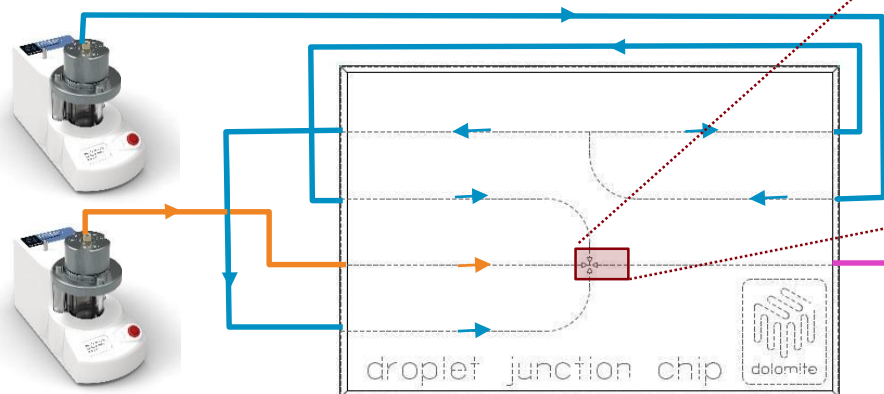
To-be-dispersed organic phase
[DMDBTDMA] = 1 M
n-dodecane

- ✓ Hydrophilic surface, suited for oil in water segmented flow

Sketch of the 100 μ m ID hydrophilic FF-junction chip



Microchannel dimensions:
Width : 300 μ m
Depth : 100 μ m



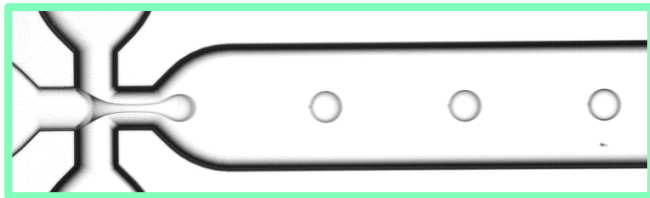
Dolomite®
Pumps



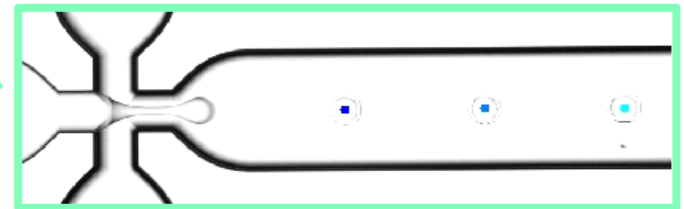
Syrris®
Membrane phase separator

Droplets morphometry and velocimetry analysis [6]

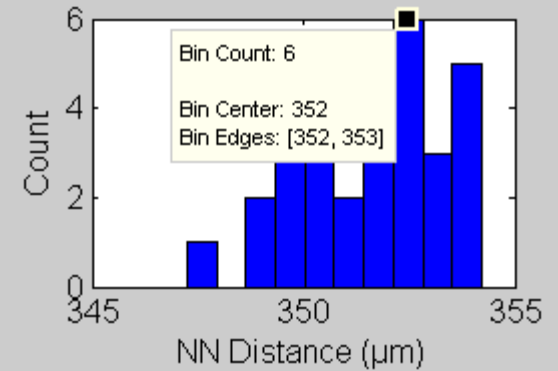
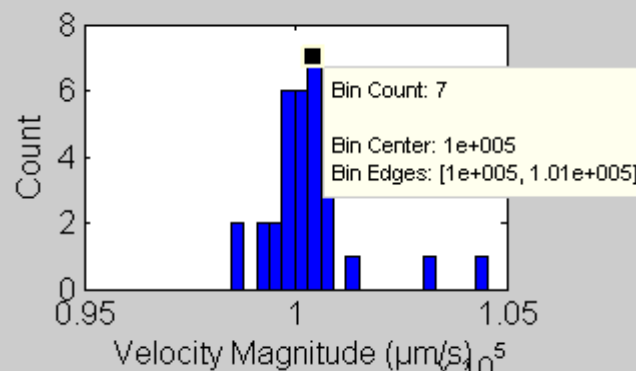
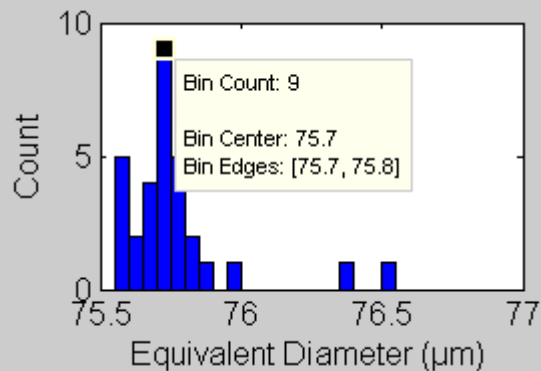
RAW VIDEO



SOFTWARE TREATMENT



10.000 fps acquisition – 94 ms
 Played back at 30 fps
 Slowed down by a factor >300
 Number of droplets analysed: 31



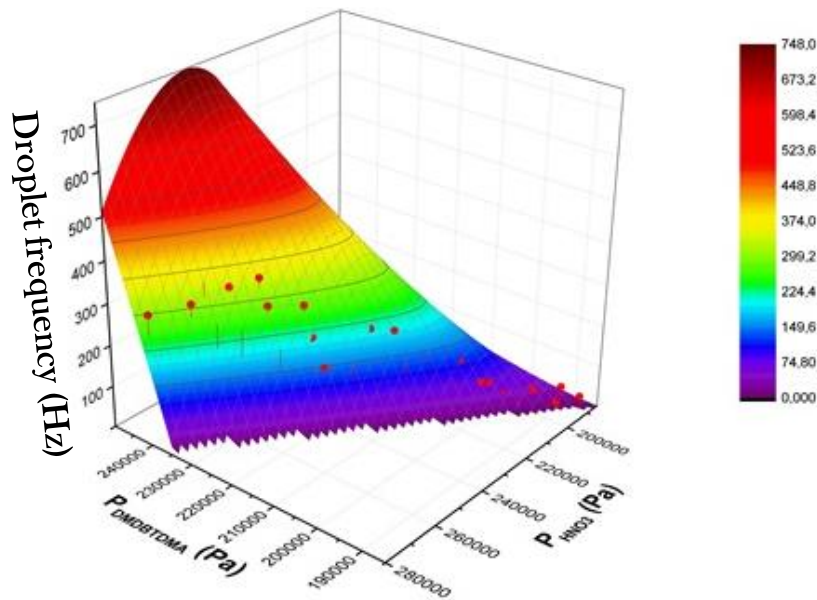
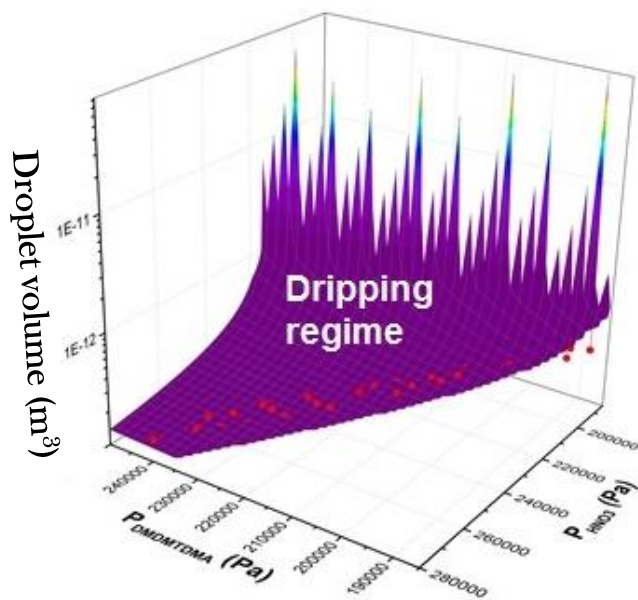
Experiments performed on 2016/11/22 with phase separation – P_{HNO_3} = 1280 mPa – P_{DMBDTMA} = 1180 mPa

Droplets diameter

Droplets velocity

Droplets spacing

Results comparison with Cubaud et al. theoretical model [5]

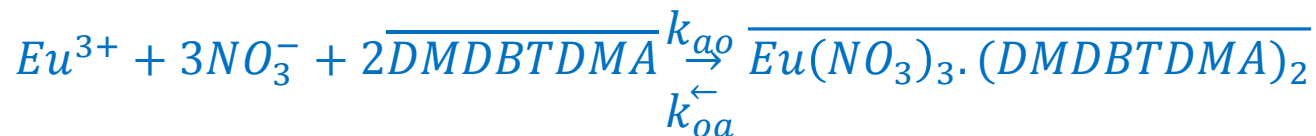


Theoretical and experimental comparison of the droplets populations characteristics generated in a FF-junction in the dripping regime, for the following chemical system : $[Eu(III)] = 10^{-2}M$ – $[HNO_3] = 4M$ / $[DMDBTDMA] 1M$ – n-dodecane

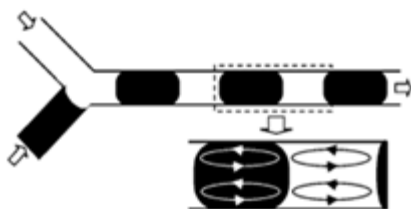


**Predicted volumes and frequencies
= Hydrodynamics control**

MASS TRANSFER STUDY



$$K_D = \frac{C_{org,eq}}{C_{aq,eq}} = \frac{k_{ao}}{k_{oa}}$$



With segmented flows, diffusion is not a limiting factor in mass transfer:
The **regime** is called « **kinetic** » [7]

Mass transfer is only ruled by reaction kinetics



$$\frac{dC_{aq}}{dt} = \left(\frac{A}{V} \right) (k_{oa} C_{org} - k_{ao} C_{aq})$$

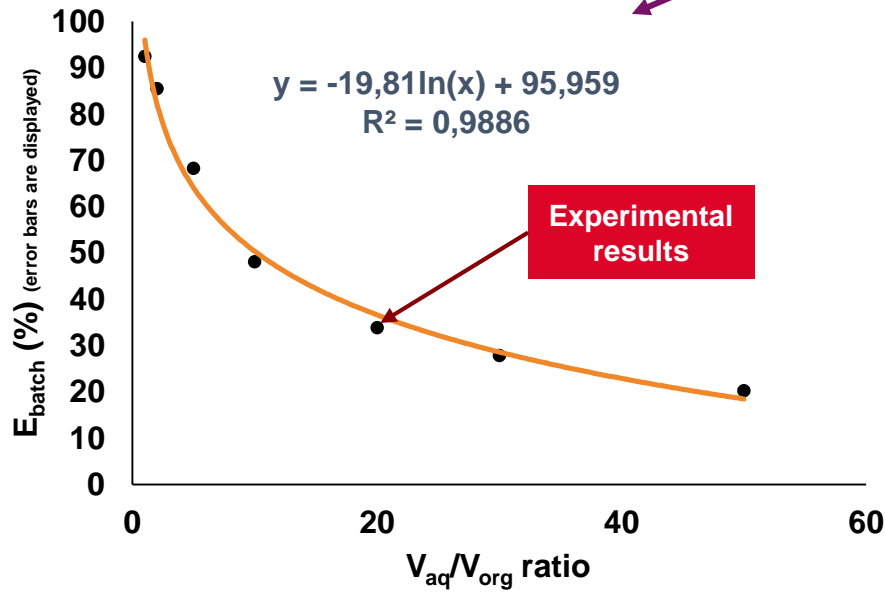
hence

$$E\%(t) = E_{batch} \left(1 - e^{-\frac{A}{V} \left(1 + \frac{1}{K_D} \right) k_{ao} t} \right)$$

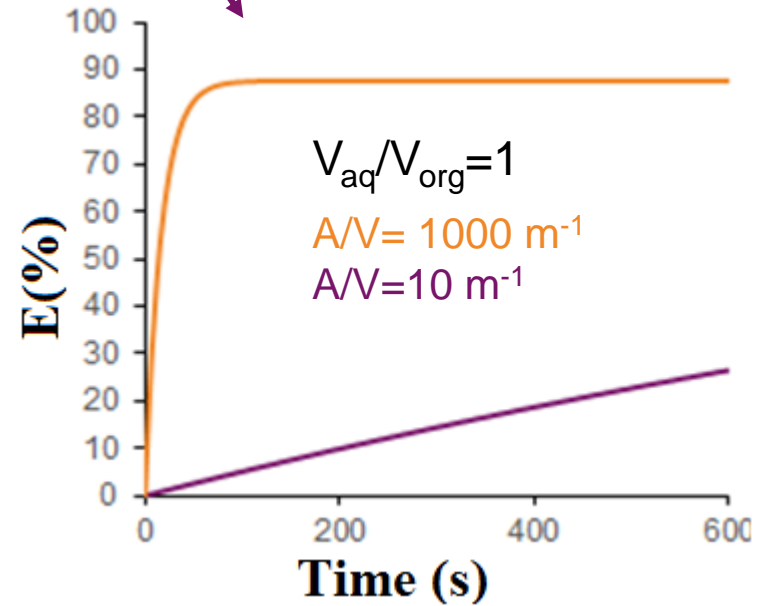
$$t \rightarrow +\infty \text{ then } E\% \rightarrow E_{batch}$$

Composition of the extraction yield

$$E\%(t) = E_{batch} \left(1 - e^{-\frac{A}{V} \left(1 + \frac{1}{K_d} \right) k_{aot} t} \right)$$

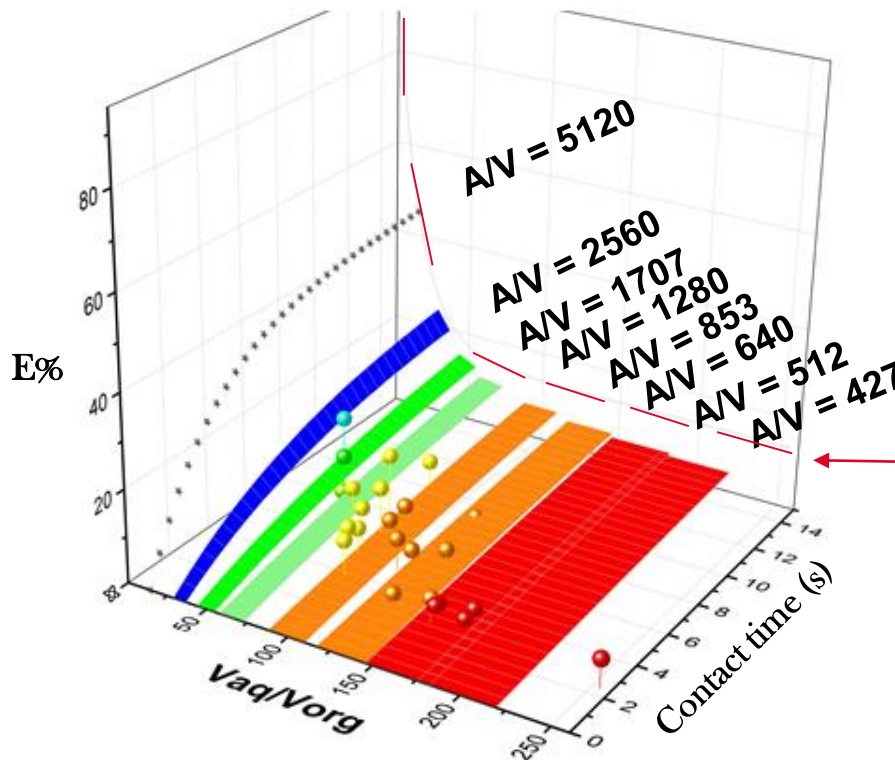


➔ The extraction yield is dependent on the volume ratio of the two phases.



➔ And on the specific interfacial area

MASS TRANSFER CASE STUDY: EU(III) EXTRACTION BY MALONAMIDE DMDBTDMA



$$K_d = 9.1 \pm 0.3$$

$$k_{ao} \sim (5.9 \pm 0.7) \cdot 10^{-5} \text{ m/s} \quad [8]$$

$$E_{batch} = E_{\infty} = f\left(\frac{V_{aq}}{V_{org}}\right)$$

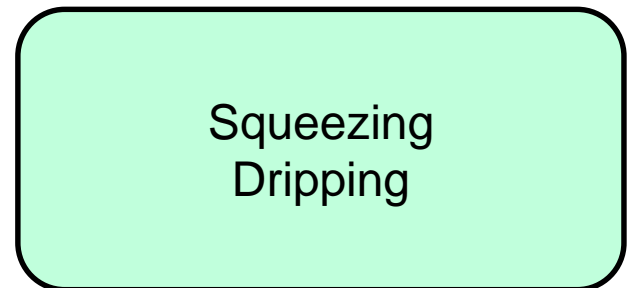
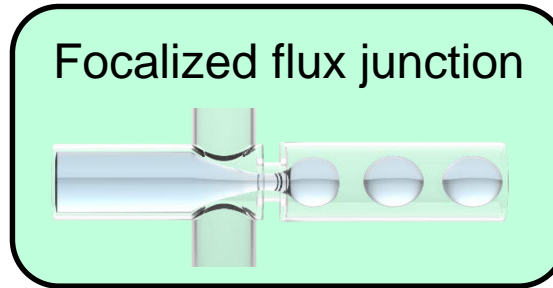
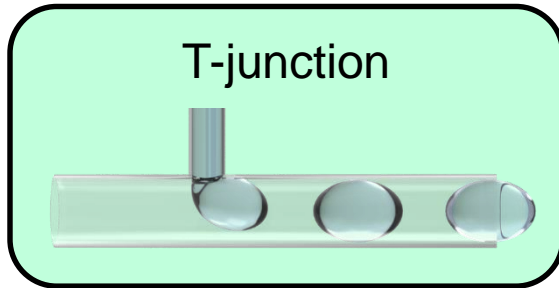
Dripping regime, Dolomite® FF junction, [Eu(III)] = 10⁻²M – [HNO₃] = 4M / [DMDBTDMA] 1M - dodecane



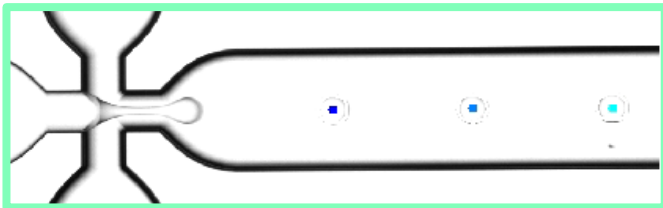
Mass transfer results currently being validated

Extraction yields are slightly superior (~5%) to those expected theoretically, due to a small uncertainty on contact times.

1. Factual background: the choice of junctions and flow regimes



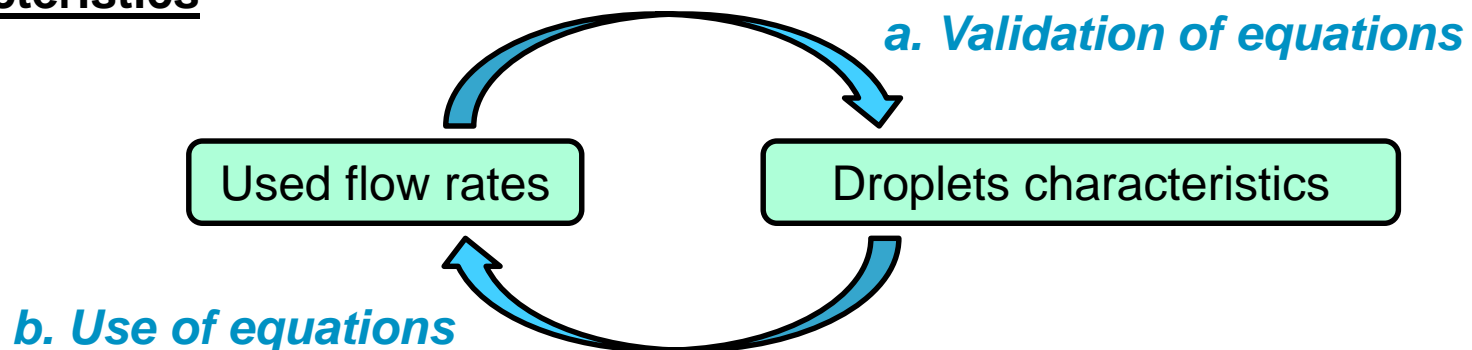
2. Development of an observation method for segmented flow characterization



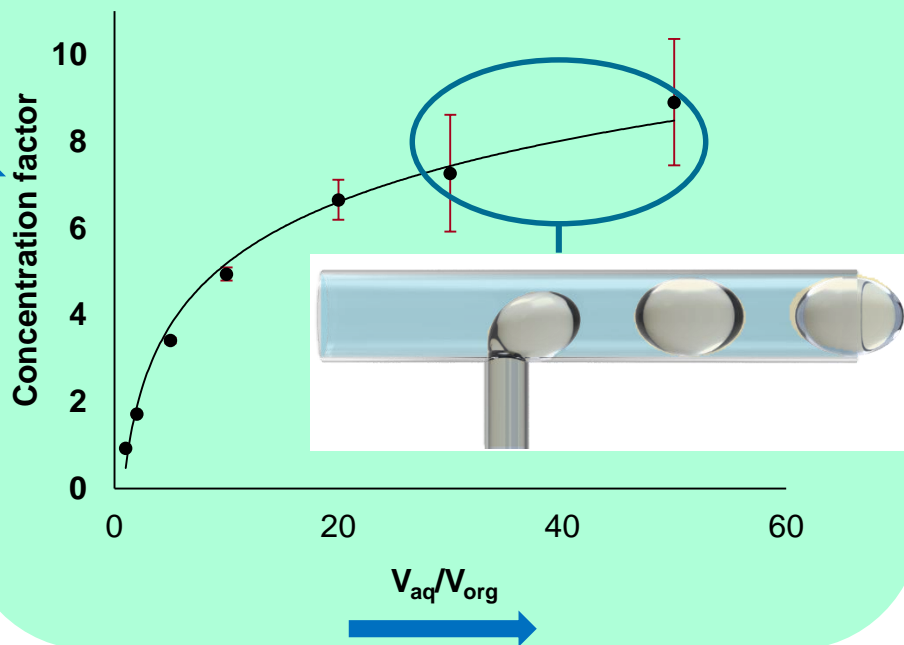
- ❖ Droplets size
- ❖ Droplets frequency
- ❖ Droplets velocity
- ❖ Spacing between droplets

✓ Quick and exhaustive analysis of any segmented flow

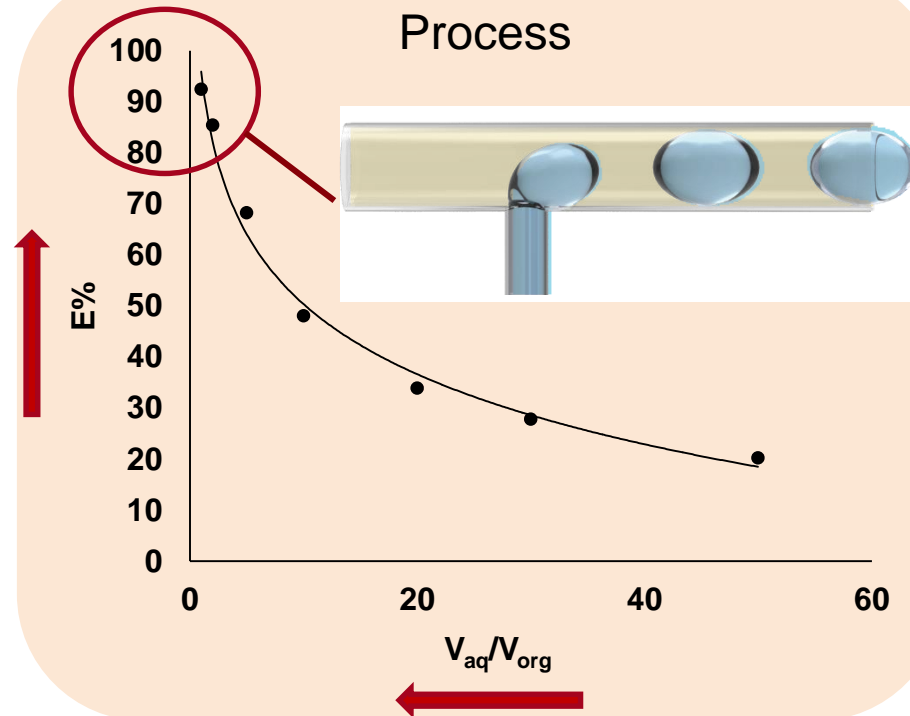
3. Validation of theoretical equations : produce droplets with desired characteristics



Analysis



Process



- ✓ FF-junction chip to be optimized
- ✓ Same methodology to be developed with T-junctions chips
- ✓ The whole approach was based on one particular chemical system :

HNO_3 4M – Eu 10^{-2} M / Dodecane – DMDBDMDMA 1M

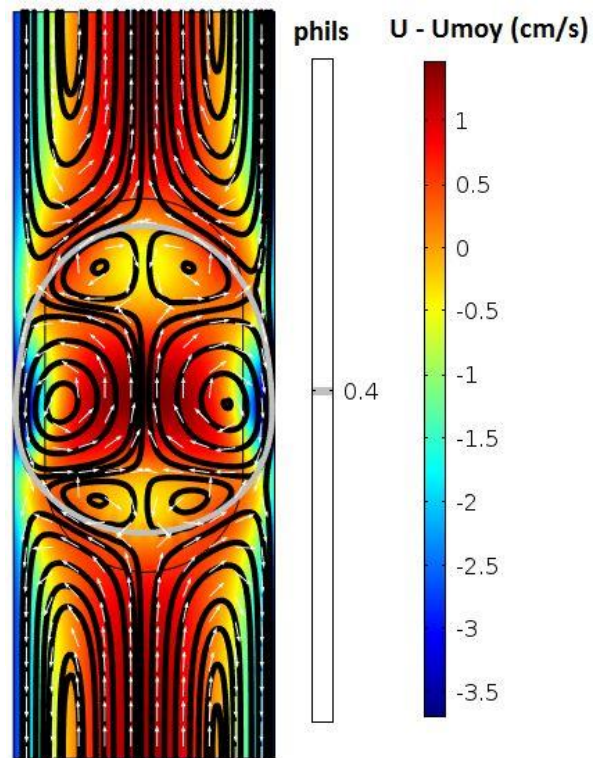
Slow kinetics, $\frac{\eta_{org}}{\eta_{aq}} \sim 15$

- ✓ Have a generic approach towards mass transfer, independent on the used junction or the chemical system
- ✓ COMSOL (CFD) model being developed with Chimie Paris-Tech (Pr. Cavadias and Pr. Cote):
- *mass transfer model between a droplet and an external phase being tested*

« Circulation can provide a powerful boost to the inter-phase mass transfer »

Burns and Ramshaw,
Lab Chip 1 (1):10–5,
2001

COMSOL
MULTIPHYSICS®





Thank you
for your
attention

ORALS

- *Liquid-Liquid Extraction of two Radiochemical Systems at Micro-Scale: Predict and Achieve Segmented Flow to Optimize Mass Transfer*
AnalytiX-2017, March 22-24, 2017, Fukuoka (Japan)

POSTERS

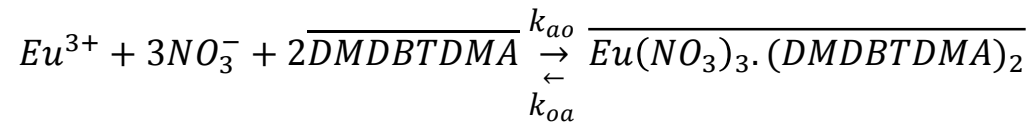
- *Liquid-Liquid microflow patterns of two radiochemical systems used in the nuclear field: predict the formation of segmented flow*
RANC 2016, April 10-15, 2016, Budapest (Hungary)
- *Predict and compare the formation of segmented flow in microsystems : Interest for radiochemical liquid-liquid extraction*
DEFI 2016, October 12-13, 2016, Lyon (France)

PAPERS

- *A Simple and Adaptive Methodology to use Commercial Microsystem as Screening Tool: Validation with the U-TBP Chemical System*
Solvent Extraction Ion Exchange

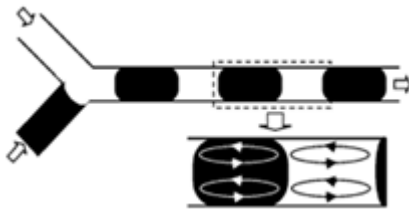
Model	Regime	Formula
Liu	Transition	$\frac{l_{plot}}{w_c} = (\tilde{\varepsilon} + \tilde{\alpha} \frac{Q_d}{Q_c}) Ca_c^{\tilde{m}}$ $\tilde{\varepsilon} = 0.32, \tilde{\alpha} = 0.219$ et $\tilde{m} = -0.243$
Cubaud	Dripping	$\frac{l_{plot}}{h} \approx \begin{cases} 2.2 \cdot 10^{-4} \left(\frac{1}{1+\phi} Ca_c \right)^{-1} & \text{pour } \frac{l_{plot}}{h} > 2.5 \\ 0.5 \left(\frac{1}{1+\phi} Ca_c \right)^{-0.17} & \text{pour } \frac{l_{plot}}{h} < 2.5 \end{cases}$
Fu		$\frac{l_{plot}}{h} \approx \begin{cases} 0.3 \phi^{0.23} Ca_c^{-0.42} & \text{pour } \frac{l_{plot}}{h} > 2.35 \\ 0.72 \phi^{0.14} Ca_c^{-0.19} & \text{pour } \frac{l_{plot}}{h} < 2.35 \end{cases}$
Cubaud	Jetting	$\frac{d}{h} \approx 2.19 \sqrt{\phi}$

MASS TRANSFER STUDY



$$K_D = \frac{C_{org,eq}}{C_{aq,eq}} = \frac{k_{ao}}{k_{oa}}$$

With $K_d = 9.1 \pm 0.3$ and $k_{ao} \sim (5.9 \pm 0.7) \cdot 10^{-5}$ m/s [7]



With segmented flows, diffusion is not a limiting factor in mass transfer: The **regime** is called « **kinetic** »^[5]

Mass transfer is only ruled by reaction kinetics

$$\frac{dC_{aq}}{dt} = \left(\frac{A}{V}\right)(k_{oa}C_{org} - k_{ao}C_{aq}) \quad \text{hence}$$

$$\ln\left(1 - \left(\frac{C_{aq}}{C_{aq,eq}}\right)\right) = -\frac{A}{V}\left(1 + \frac{1}{K_d}\right)k_{ao}t$$

$$\text{Yet } R_{extraction}(t) = \frac{C_{aq,0} - C_{aq}(t)}{C_{aq,0}}$$

$$R_{extraction}(t) = R_{batch} \left(1 - e^{-\frac{A}{V}\left(1 + \frac{1}{K_d}\right)k_{ao}t}\right)$$

$t \rightarrow +\infty$ then $R_{extraction} \rightarrow R_{batch}$