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

A. Vansteene, J. P. Jasmin, R. Brennetot, C. Mariet, S. Cavadias, G. Cote

DE LA RECHERCHE À L'INDUSTRIE

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

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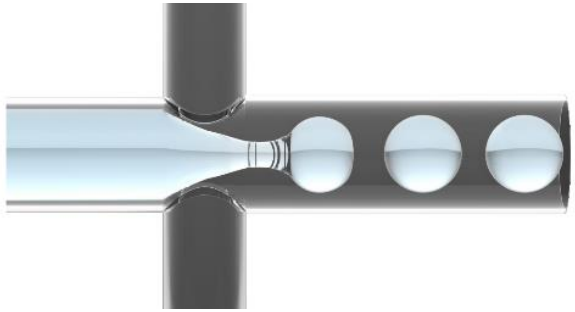
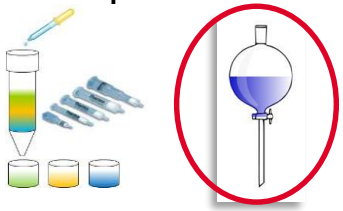


PhD thesis started in November, 2015

OVERVIEW : RADIOCHEMICAL ANALYSIS

Current nuclear procedures :

- Separation and purification is needed before detection

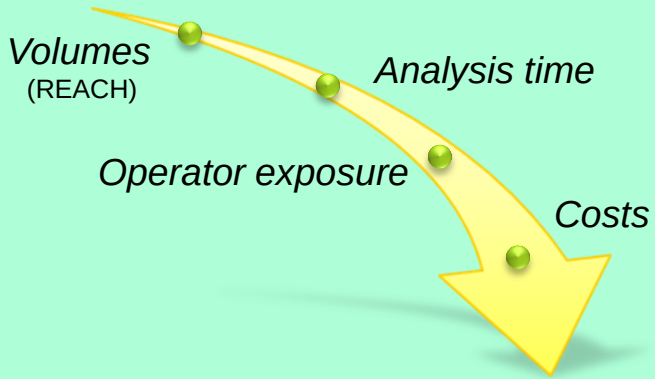


- Hardly implementable in glove boxes
- Huge volumes of solvents

➢ **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]



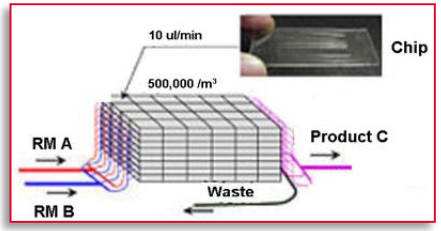
Classical fluid dynamics

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

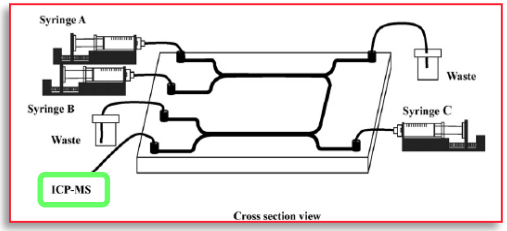
LIQUID-LIQUID EXTRACTION MINIATURISATION (µ-LLE)

Assets

- Analysis automation and parallelization
- Possible coupling with detection devices



Ralston, ISEC Conference, *2011*



Kagawa, Talanta, *2009, 79, 1001*

Two types of biphasic flows

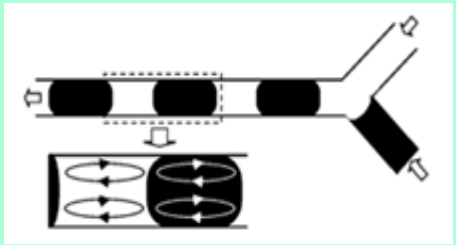
Parallel flows (stratified flows)

✓ 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

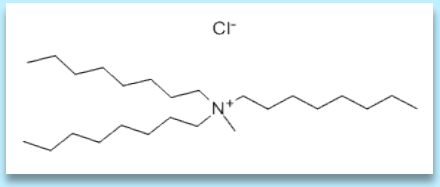
Quick kinetics [2]

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)



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

Viscosity ratio

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

Eu(III) / DMDBTDMA

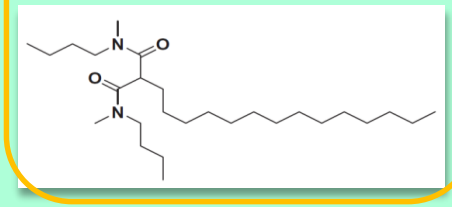
Slow kinetics [3]

Aqueous phase :

[Eu(III)]= 10^{-2} M
[HNO_3]= 4 M

Organic phase :

[DMDBTDMA]= 1 M
***n*-dodécane**



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

Viscosity ratio

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

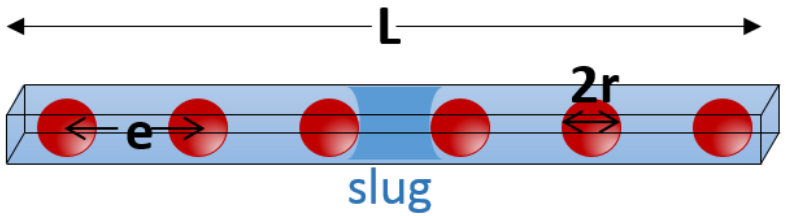
[2] Coleman et al., AIME Annual Meeting, 1979, New Orleans, LA, USA
[3] Weigl et al., Solv. Ext. Ion Exch., 2001, 19, 215-229

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

PHD AIMS AND OBJECTIVES

▶ Optimize the specific interfacial area (A/V) = $\frac{Interfacial\ area}{Microchannel\ volume}$

Determine the segmented flow (i.e. droplets population) characteristics, in order to figure out the specific interfacial area



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

Physicochemistry	Hydrodynamics	Chip geometry
η_i, σ	Q_i	$Junction\ type\ (T, FF), dimensions$

JUNCTION TYPE

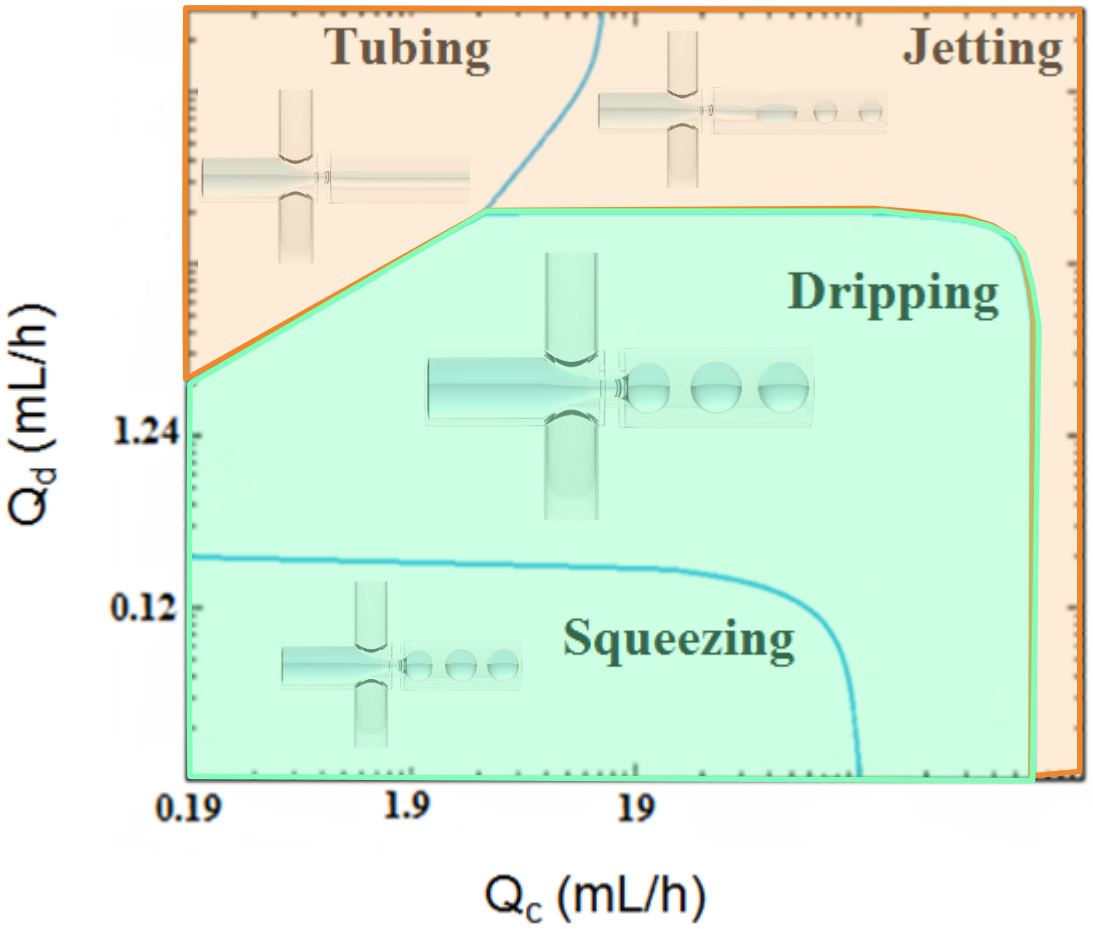
Which junction best suits our needs?

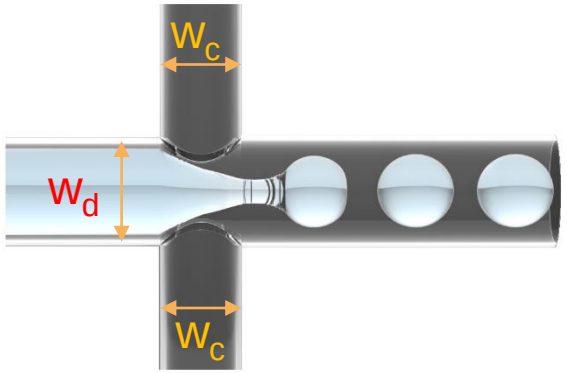
 T-Junction	❑ Available equations for every flow regime ❑ Squeezing, transition regime, and dripping regimes to be studied
 Focalized Flux (FF)	❑ Available equations for every flow regime ❑ Squeezing, transition regime, and dripping regimes to be studied
 Co-current Flux	❑ Very few models in the litterature

► Flow regimes to be chosen

*Will only be presented in the following our results concerning **the FF junction***

FLOW CARTOGRAPHY – FF JUNCTION





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

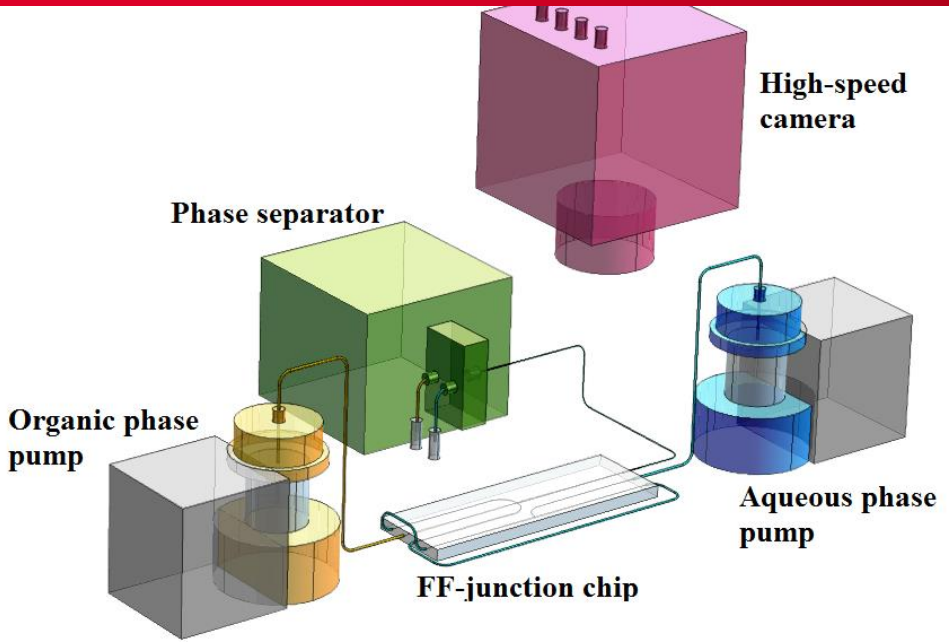
- Squeezing
- Dripping

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



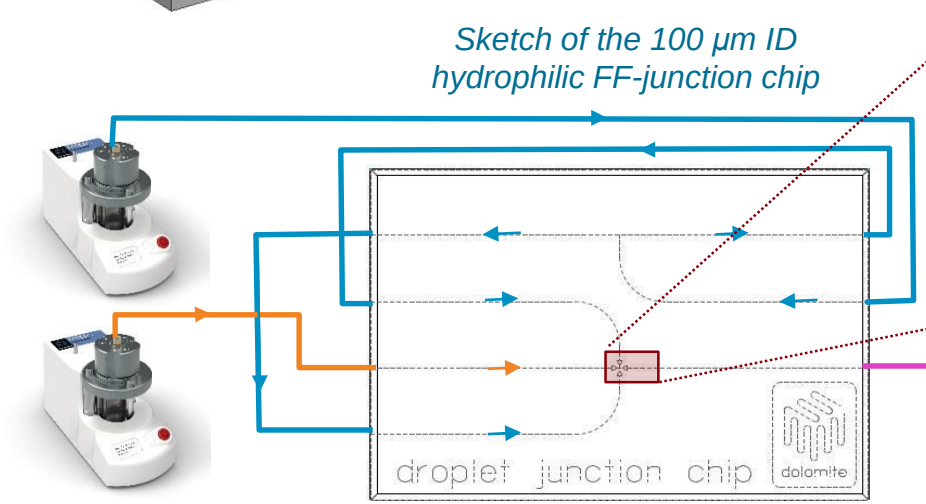
- Glass chip (Dolomite, UK)

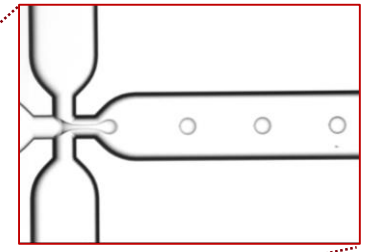
✓ Corrosive chemicals (Acids, solvents)

Continuous aqueous phase	To-be-dispersed organic phase
[Eu(III)]= 10^{-2} M	[DMDBTDMA]= 1 M
[HNO_3]= 4 M	*n*-dodecane

✓ Hydrophilic surface, suited for oil in water segmented flow

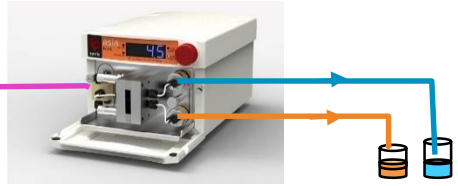
Sketch of the 100 µm ID hydrophilic FF-junction chip





Microchannel dimensions:
Width : 300 µm
Depth : 100 µm

Dolomite®
Pumps

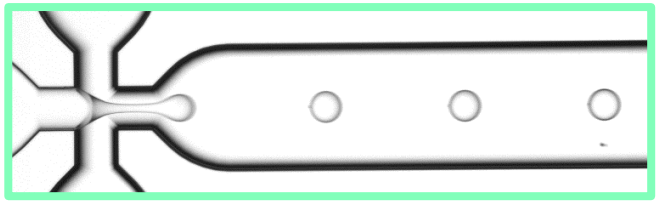


Syrris®
Membrane phase separator

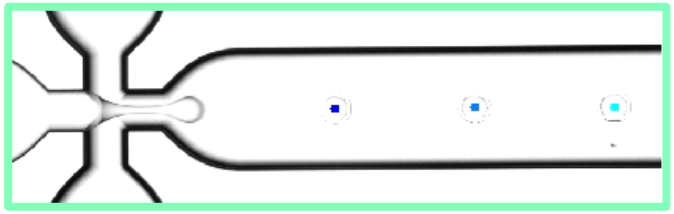
ACQUISITION METHOD FOR DROPLETS POPULATION CHARACTERISTICS

Droplets morphometry and velocimetry analysis [6]

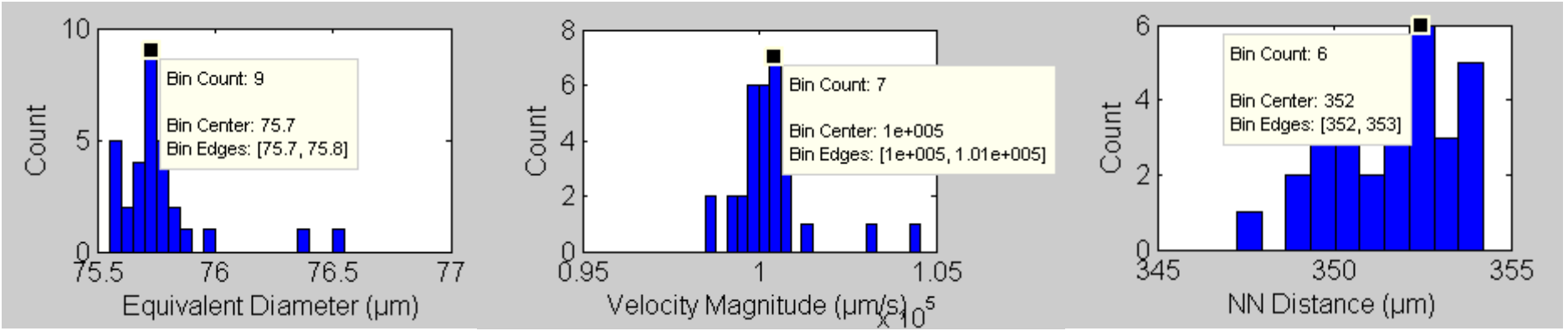
RAW VIDEO



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_{HNO3}= 1280 mPa – $P_{DMDBTDMA}$= 1180 mPa

Droplets diameter

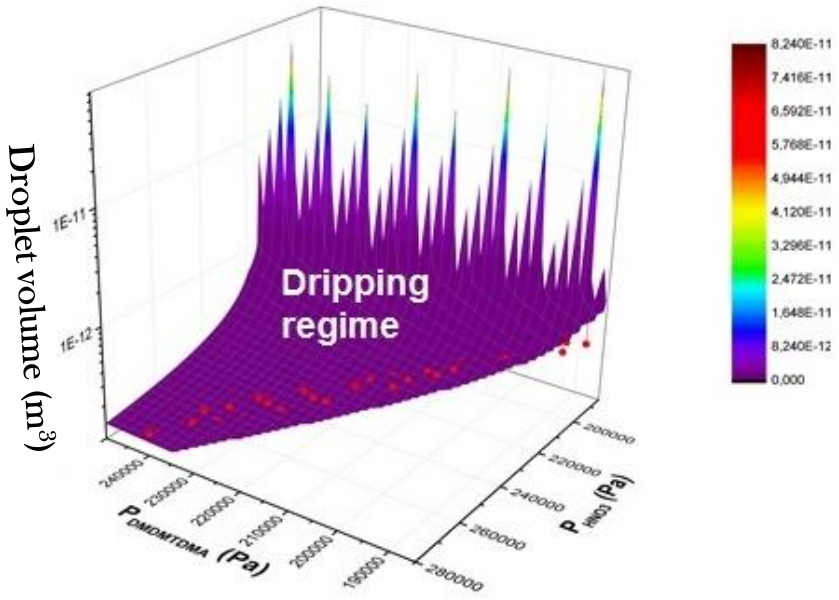
Droplets velocity

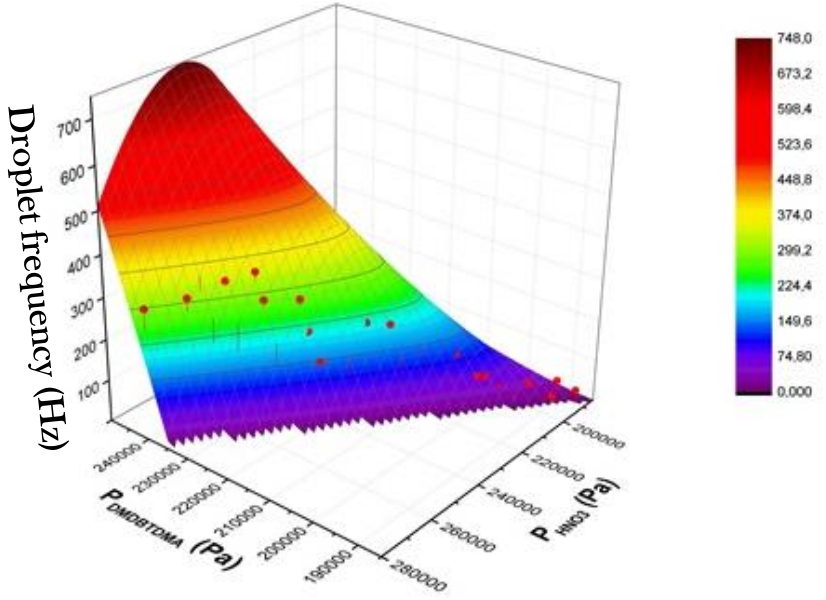
Droplets spacing

[6] Basu, *Lab Chip*, 2013, 13, 1892

VALIDATION OF THE DRIPPING MODEL

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

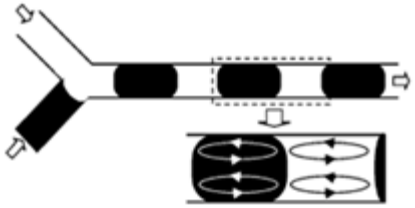
➡ **Predicted volumes and frequencies = Hydrodynamics control**

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

MASS TRANSFER STUDY

$$Eu^{3+} + 3NO_3^- + 2\overline{DMDBTDMA} \underset{k_{oa}^{\leftarrow}}{\overset{k_{ao}}{\rightleftarrows}} \overline{Eu(NO_3)_3.(DMDBTDMA)_2}$$

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



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

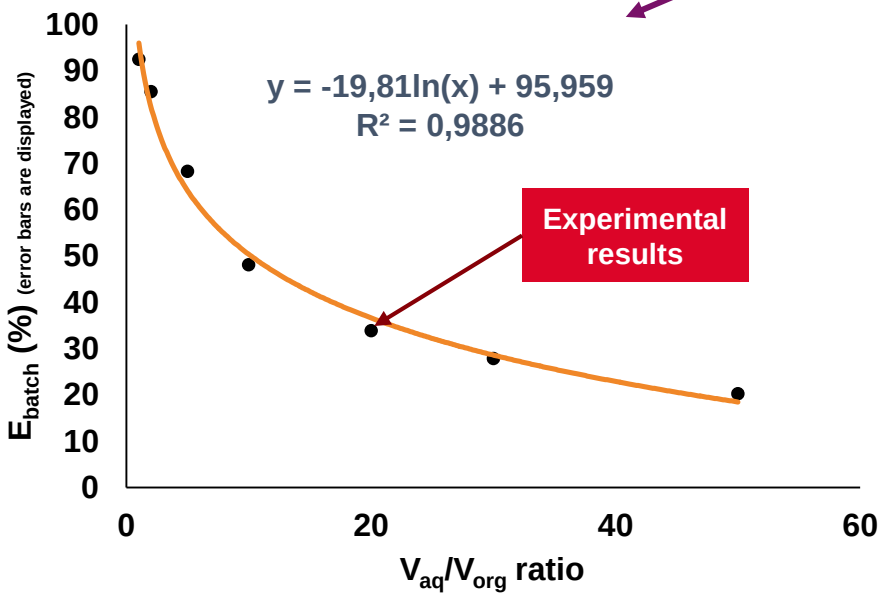
$$E\%(t) = E_{batch}\left(1 - e^{-\frac{A}{V}\left(1+\frac{1}{K_d}\right)k_{ao}t}\right)$$

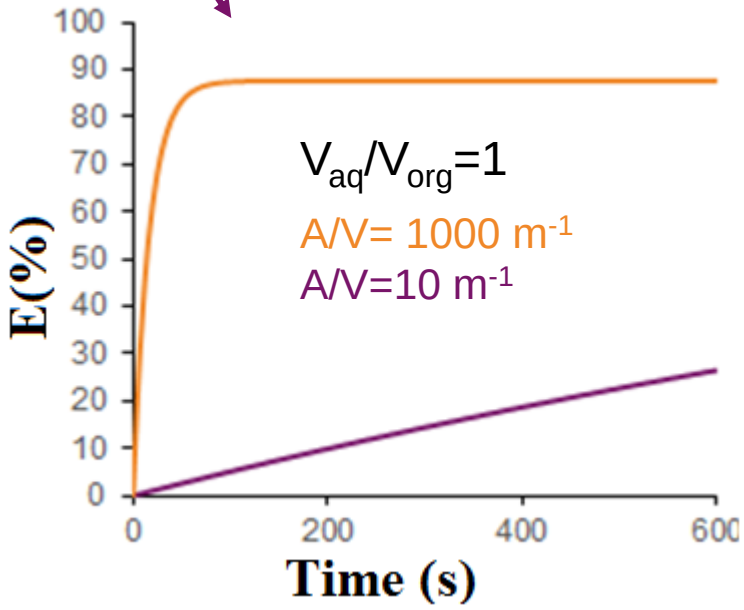
$$t \to +\infty \; then \; E\% \to E_{batch}$$

[7] Launière, Gelis, *ACS*, 2016, 55, 2272-2276

Composition of the extraction yield

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

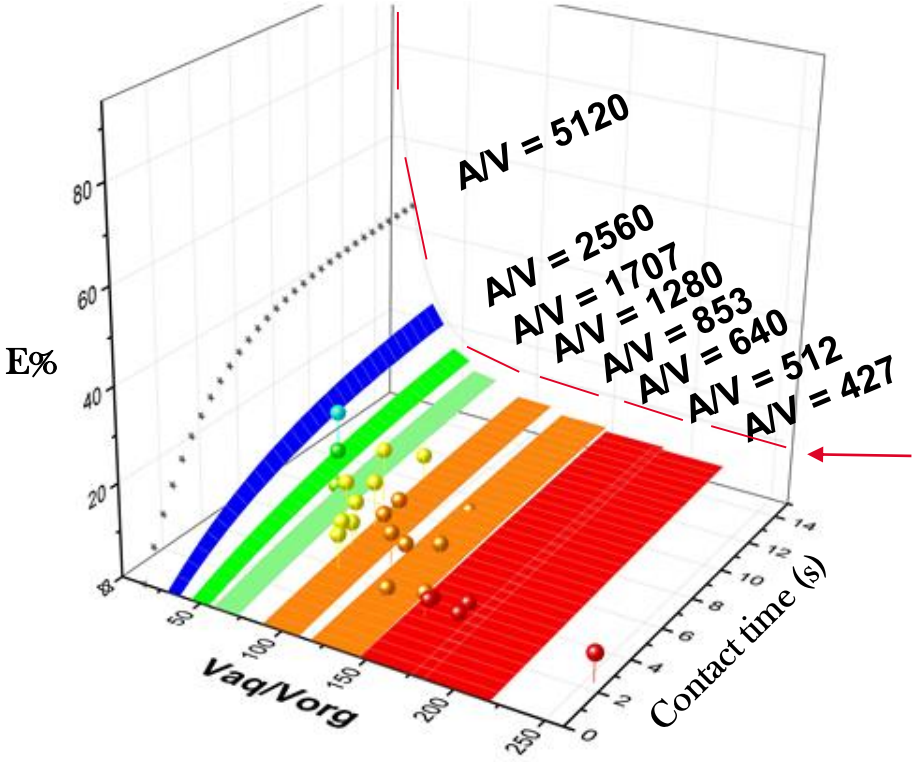




The extraction yield is dependent on the volume ratio of the two phases.

And on the specific interfacial area

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



$K_d = 9.1 \pm 0.3$

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

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

Dripping regime, Dolomite® FF junction, [Eu(III)]= 10^{-2}M – [HNO_3]=4M /[DMDBTDMA] 1M - dodecane

Mass transfer results currently being validated

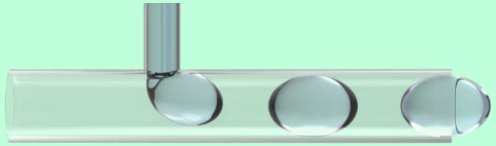
Extraction yields are slightly superior (~5%) to those expected theoretically, due to a small uncertainty on contact times.

[8] Hellé et al. Microfluidics and nanofluidics 19(5) 1245-1257, 2015

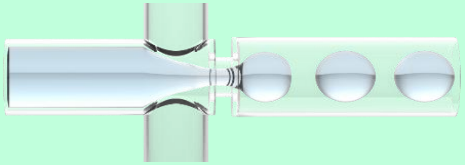
CONCLUSION

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

T-junction

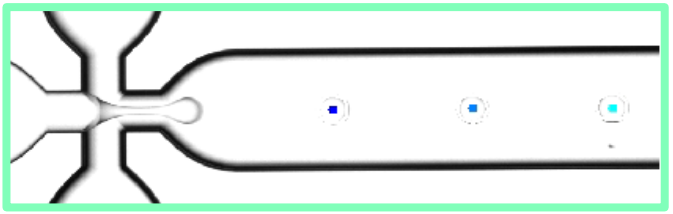


Focalized flux junction



Squeezing
Dripping

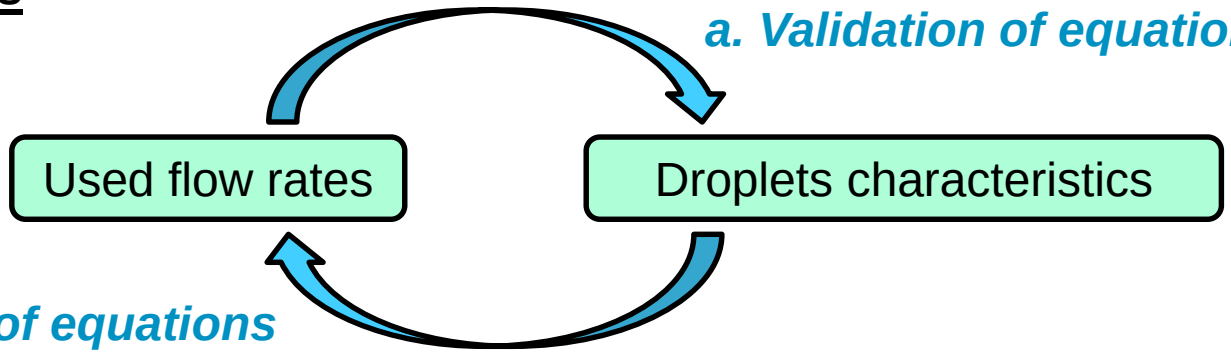
2. Development of an observation method for segmented flow characterization



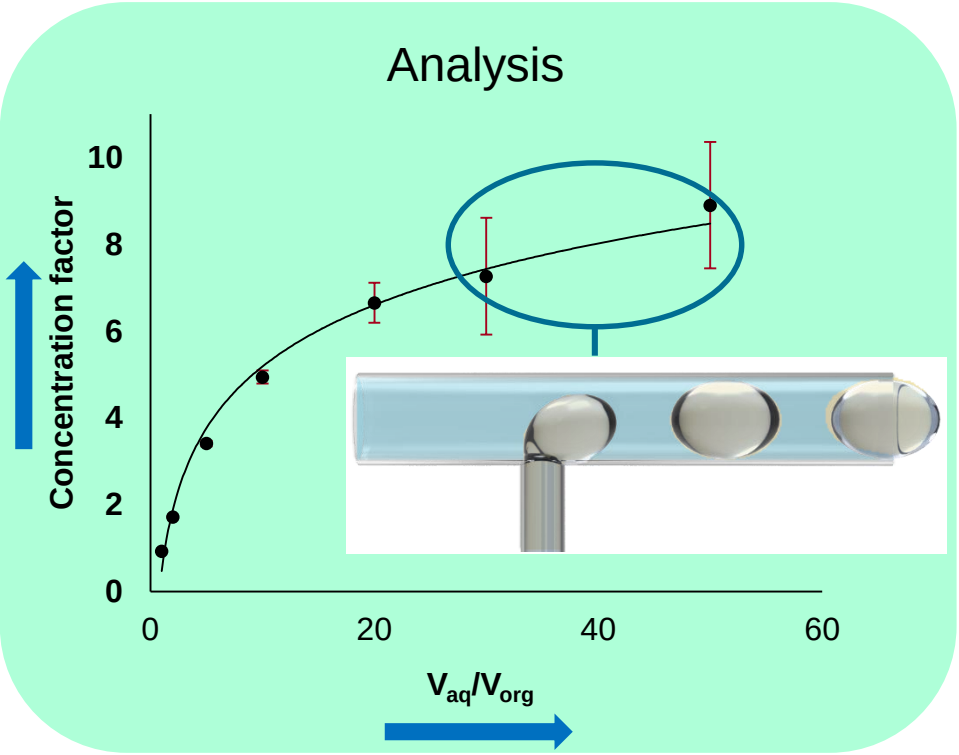
- Droplets size
- Droplets frequency
- Droplets velocity
- Spacing between droplets

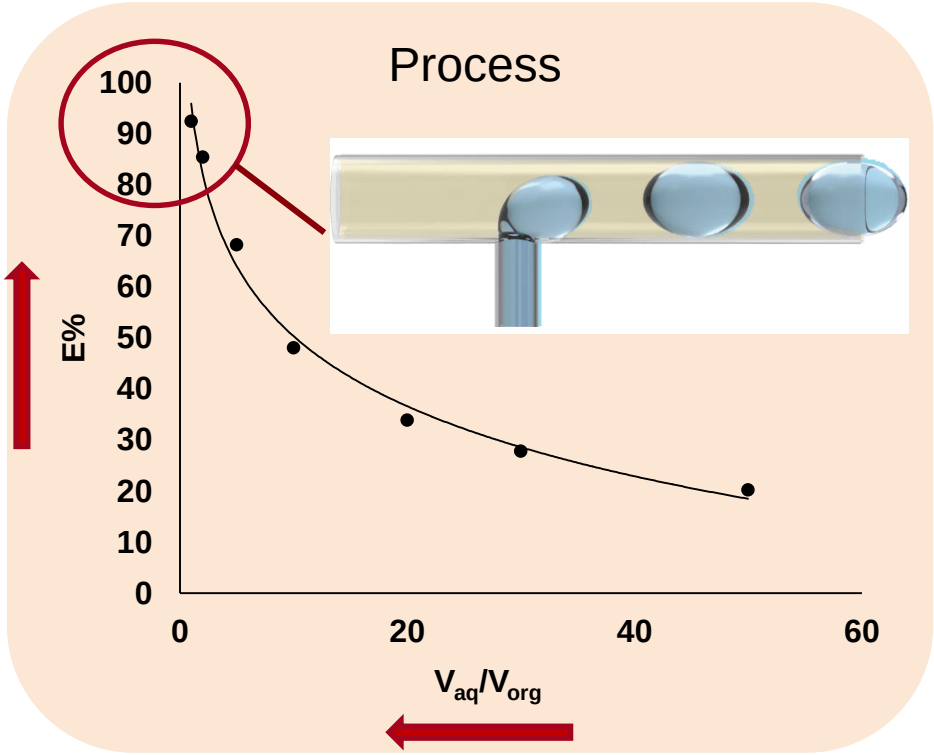
✓ Quick and exhaustive analysis of any segmented flow

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



PERSPECTIVES





- ✓ 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 – DMDBDTDMA 1M

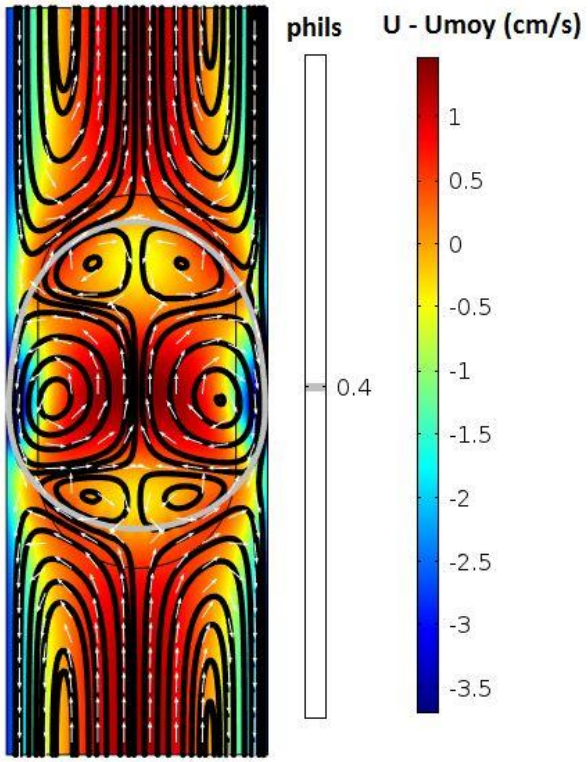
Slow kinetics, $\frac{\eta_{org}}{\eta_{aq}} \sim 15$

PERSPECTIVES

- ✓ 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 Chip1(1):10−5, 2001



COMSOL MULTIPHYSICS®

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

FORMULAE – CROSS JUNCTIONS

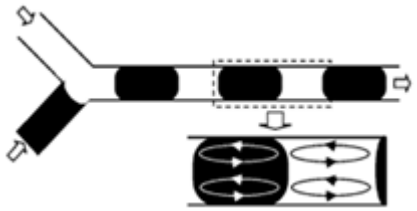
Model	Regime	Formula
Liu	Transition	$\frac{l_{plot}}{w_c} = (\tilde{\varepsilon} + \tilde{\alpha}\frac{Q_d}{Q_c})Ca_c^{\tilde{m}}$ $\quad \tilde{\varepsilon} = 0.32, \tilde{\alpha} = 0.219 \; et \; \tilde{m} = -0.243$
Cubaud	Dripping	$\frac{l_{plot}}{h} \approx \begin{cases} 2.2.10^{-4}\left(\frac{1}{1+\phi}Ca_c\right)^{-1} \; pour \; \frac{l_{plot}}{h} > 2.5 \\ 0.5\left(\frac{1}{1+\phi}Ca_c\right)^{-0,17} \; pour \; \frac{l_{plot}}{h} < 2.5 \end{cases}$
Fu		$\frac{l_{plot}}{h} \approx \begin{cases} 0.3\phi^{0.23}{Ca_c}^{-0.42} pour \; \frac{l_{plot}}{h} > 2.35 \\ 0.72\phi^{0.14}{Ca_c}^{-0.19} pour \; \frac{l_{plot}}{h} < 2.35 \end{cases}$
Cubaud	Jetting	$\frac{d}{h} \approx 2.19\sqrt{\phi}$

MASS TRANSFER STUDY

$$Eu^{3+} + 3NO_3^- + 2\overline{DMDBTDMA} \underset{k_{oa}}{\overset{k_{ao}}{\rightleftarrows}} \overline{Eu(NO_3)_3.(DMDBTDMA)_2}$$

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

With K_d = 9.1 ± 0.3 and k_{ao} ~ (5.9 ± 0.7).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

$$\frac{dC_{aq}}{dt} = \left(\frac{A}{V}\right)(k_{oa}C_{org} - k_{ao}C_{aq}) \qquad \textit{hence} \qquad \ln\left(1 - \left(\frac{C_{aq}}{C_{aq.eq}}\right)\right) = -\frac{A}{V}\left(1 + \frac{1}{K_d}\right)k_{ao}t$$

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

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

$t \to +\infty$ *then* $R_{extraction} \to R_{batch}$

[[5] Launière, Gelis, *ACS*, 2016, 55, 2272-2276