Prediction of the formation of segmented flow in microsystems for radiochemical liquid-liquid extraction

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

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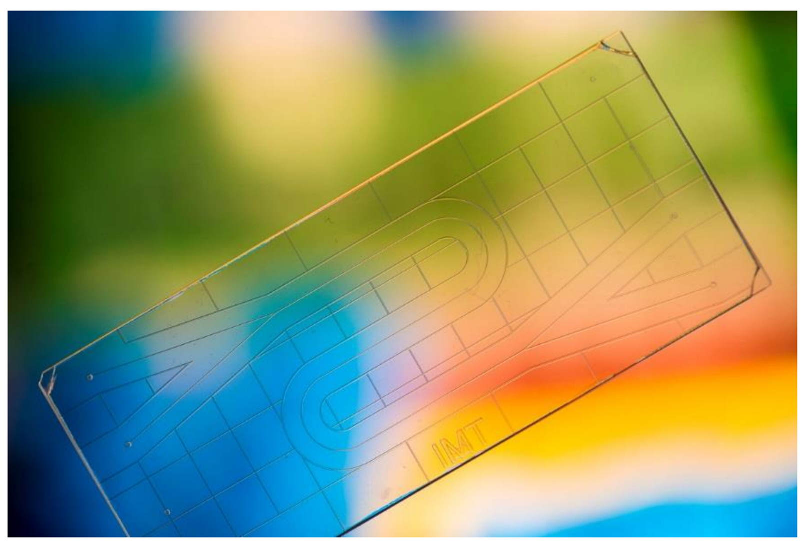
One of the most important separation techniques in radiochemical procedures is solvent extraction. It involves concentrated acids and corrosive solvents that require microsystems built with robust materials. In the last decade, a growing interest in its use in microsystems has emerged because such systems 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.

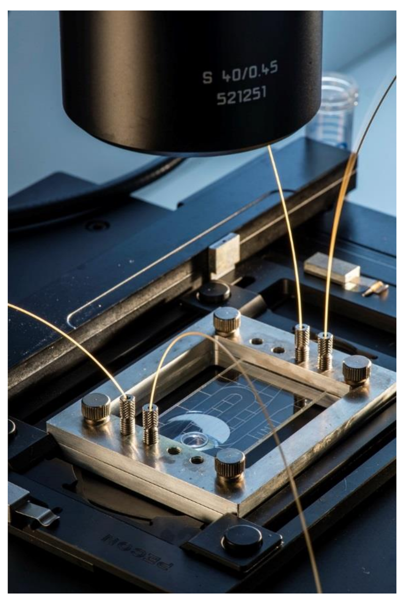
OVERVIEW

Advantages of microsystems

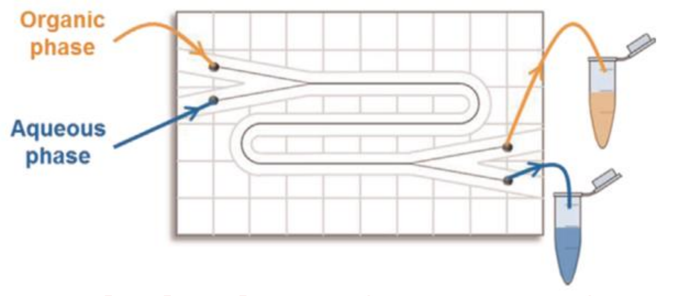
- ❑ Volume reduction (from mL to µL)
- ❑ Low operators' exposure to
  - chemicals
  - radiations

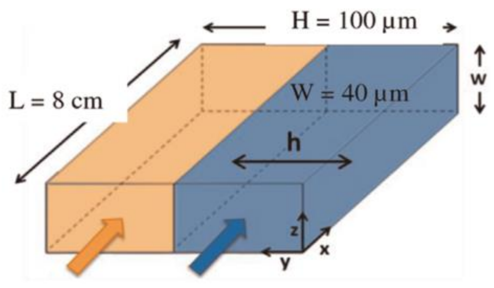
- ❑ Short analysis time
- ❑ High efficiency
- ❑ Cost reduction





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

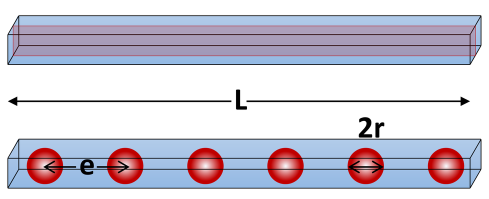
↳ **Not suitable for low kinetic systems.**

[1] Helle G et al. Talanta, 2015, 139: 123-131.

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

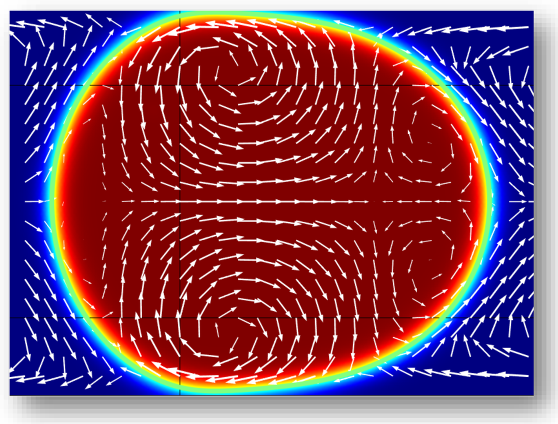


$$S_1 = Lh$$

$$S_2 = \frac{L}{e} * 4\pi r^2$$

Fig. 1 : Interface area comparison between parallel flows and droplet-based microfluidics

2. Improve mass transfer physically by recirculating species inside droplets



- Organic phase
- Aqueous phase

Fig. 2 : 2D CFD Model showing evidence of species recirculation inside 70:30 (v/v) dodecane/TBP droplets, in a continuous phase of $[HNO_3]$ = 3M / $[U(VI)]=10^{-4}$ M, with a pressure gradient of 0.66 $Pa.\mu m^{-1}$.

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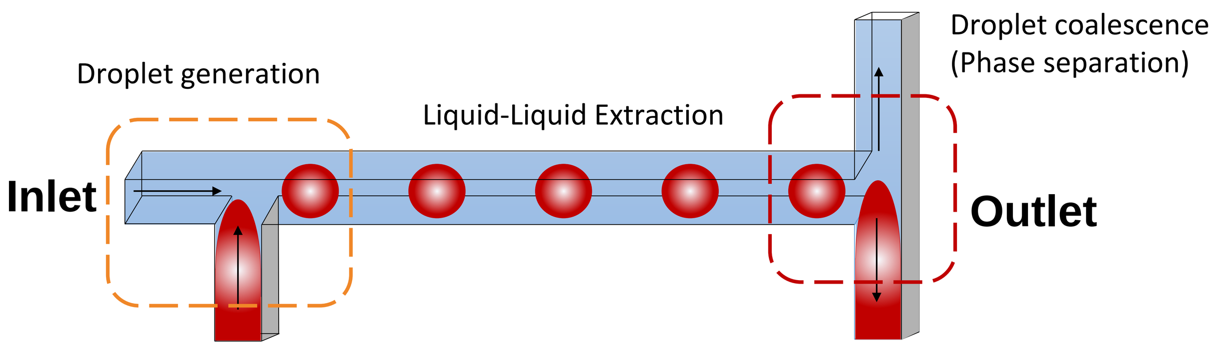
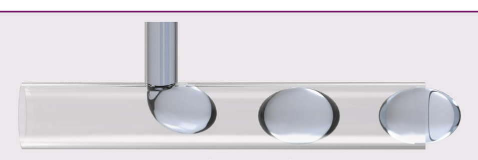
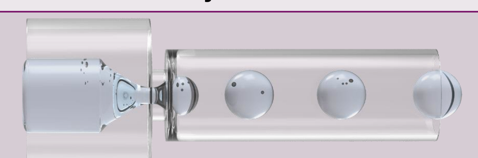
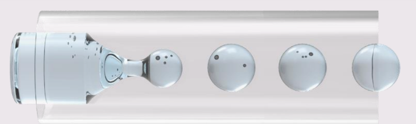
DROPLET LIFETIME

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



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

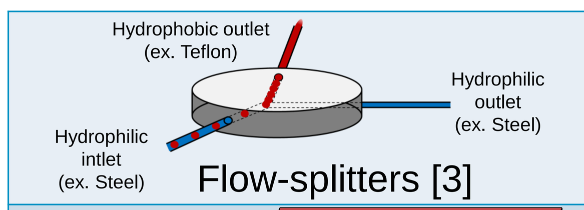
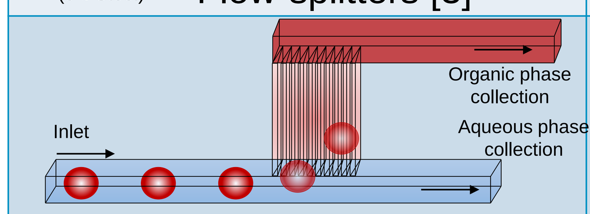
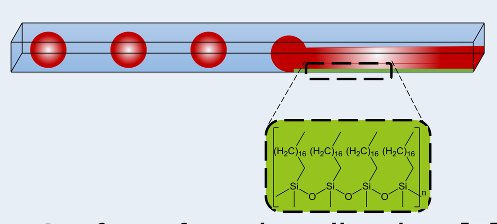
❶ DROPLET GENERATION

 T-junction	❑ Very common geometry ❑ Allows high throughput (>100Hz) 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-micron)	❑ Polydispersity ❑ Satellite droplets
 Co-flow	❑ Very high throughput droplet generation (>10kHz)	❑ 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

❷ 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 milliflows
 Hydrophobic arrays [4]	❑ Based on exploitation of capillary forces on selected materials ❑ Efficient phase separation	❑ Expensive 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

[2] Christopher GF, Anna SL, J. Phys. D: Applied Physics, 2007,40(19), R319-R336.
[3] Kashid MN et al., Ind. Eng. Chem. Res. 2007, 46, 8420-8430.
[4] Castell OK et al., Lab Chip, 2009. 9(3), 388-96.
[5] Hibara A et al., Anal. Chem., 2005, 77(3), 943-947.

MODELLING

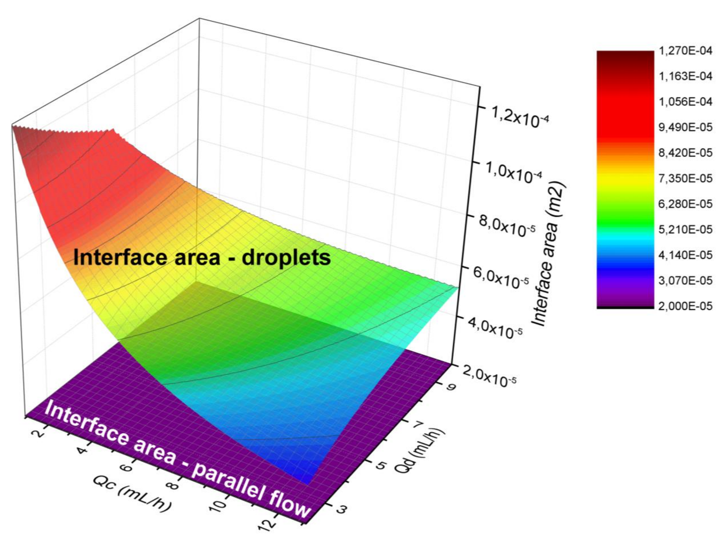


Fig. 3 : Comparison between the interface area generated in a flow-focusing geometry operating in the droplet jetting regime and parallel flow in a similar microsystem [6]

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

[6] Utada A S et al., Science, 2005, 308: 537-541.

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.

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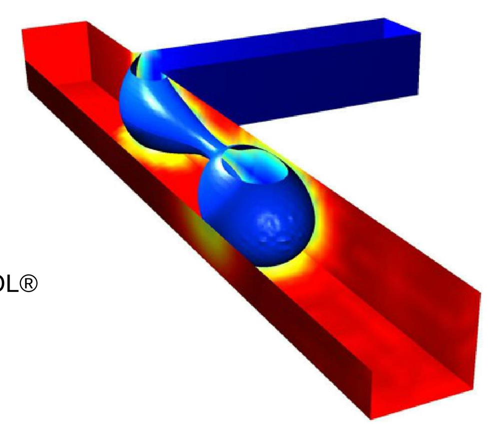

Fig. 4 : CFD simulation of multiphase flow in a T-junctionVideo accessible online at : https://www.comsol.fr/model/download/11070/droplet_breakup.swf

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.

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