

SUPPORTING INFORMATION FOR

Towards Mechanistic Understanding of Nuclear Reprocessing Chemistries by Quantifying Lanthanide Solvent Extraction Kinetics via Microfluidics with Constant Interfacial Area and Rapid Mixing

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Chemicals and Materials

All experiments were conducted using chemicals of at least analytical reagent grade, received from Fisher Scientific and Sigma-Aldrich. Bis-(2-ethylhexyl) phosphoric acid (HDEHP) was received from Alfa-Aesar and purified using a Cu salt precipitation method¹. Lanthanide stock solution was prepared using Ln nitrates of 99.99% purity.

Tubing was obtained via special order from Zeus, Inc. (1/32 inch OD, 125 $\mu\text{m} \pm 10 \mu\text{m}$ ID Teflon FEP and 1/16 inch OD, 1.2 mm $\pm 50 \mu\text{m}$ ID Teflon FEP). Tees were obtained from Swagelok, Inc. (SS Swagelok Tube Fitting, Low Dead Volume Union Tee, 1/16 in. Tube OD part number SS-1F0-3GC). Reducers were obtained from Valco Instruments Co. (Valco 1/16" to 1/32" Reducer with 1/32" bore, part number IZR1.5T)

Experimental Section

Laser machining of tubing and assembly of the device

The organic withdrawal channels were laser machined from 1/32" Teflon® FEP tubing. A Resontics RapidX 250 was utilized to machine all tubing substrates referenced within. A laser lathe stage was utilized to rotate the tubing 72° after the completion of each hole, until all 5 holes were drilled. Channel size was verified using a calibrated stereoscope. Figure S1 shows cross sections of tubing before and after machining. Figure S2 shows the details of how the device was assembled.

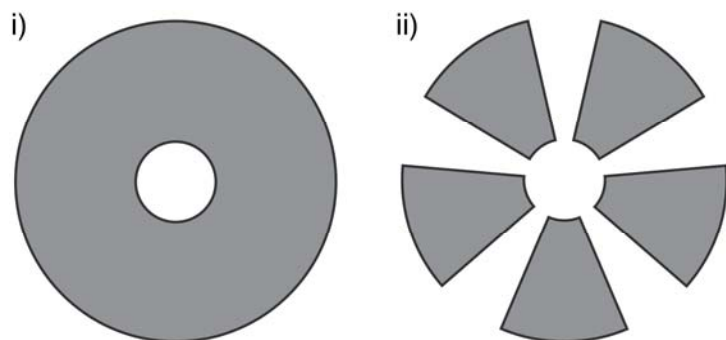


Figure S1. A cross-section of the 1/32" OD, 125 μm ID tubing i) before laser machining and ii) after laser machining. 5 holes were drilled around the circumference of the tubing using a laser lathe stage. If holes are evenly spaced, it is helpful to machine an odd number of holes so that minor over-drilling of one hole does not affect other holes. The base of each hole was machined to be $\sim 1 \times 10 \mu\text{m}$.

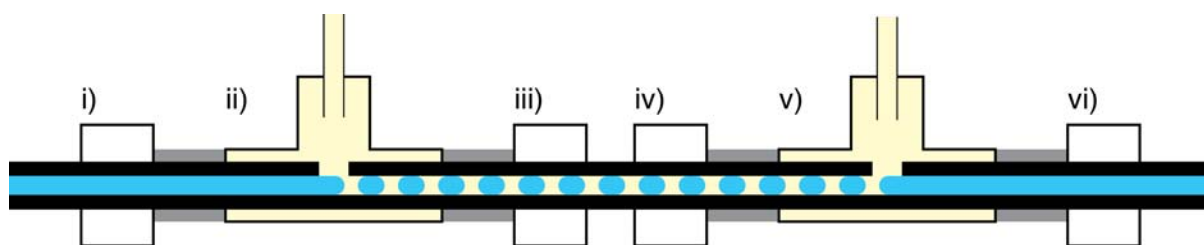


Figure S2. Details of the tubing assembly: i) Inner tubing (1/32" OD, black) containing aqueous (blue) enters a reducer (part numbers in Chemicals and Materials) to enable connection to outer tubing (1/16" OD, gray). ii) Outer tubing containing the inner tubing enters tee. Organic phase (yellow) forms droplets in inner tubing through laser machined hole. iii) An additional reducer removes the outer tubing. This piece, and the next reducer, are not necessary, but they significantly reduce dead volume in a long reaction zone. iv) Inner tubing containing aqueous/organic droplets enters a "Reducer" to enable connection to outer tubing. v) Outer tubing containing the inner tubing enters tee. Organic phase is separated through phase separator droplets in inner tubing through laser machined hole. vi) An additional reducer allows tight sealing of the tee.

Fluid properties

Surface tension measurements were made by the hanging droplet method using a Rame-Hart Instrument Co. goniometer (model 500-00 Advanced). A droplet of aqueous solution (50 mM diethylenetriamine-pentaacetic acid with 1.0 M (Na/H)₃ citrate or 1.5 M (Na/H) lactate, pH 3) was suspended in a bath of 1M HDEHP in dodecane and analyzed with DROPimage Advanced imaging software. The resulting surface tensions were 6.32 ± 0.06 and 7.66 ± 0.04 mN/m for citrate and lactate solutions, respectively, in HDEHP solution (average \pm standard error; $n = 3$

droplets per condition). An estimated value of 7 mN/m was used for predictions of critical hole size in the device (Table S1 below).

Densities used for calculating surface tensions were obtained by measuring the mass of a 10.0 μL droplet relative to the mass of a 10.0 μL droplet of Millipore water ($d = 0.99777 \text{ g/mL}$ at 22 $^{\circ}\text{C}$). All measurements were done at room temperature (22 $^{\circ}\text{C}$). The resulting densities were 1.15 ± 0.02 and $1.15 \pm 0.01 \text{ g/mL}$ for citrate and lactate solutions, respectively, and $0.89 \pm 0.03 \text{ g/mL}$ for HDEHP solution (average \pm standard deviation; $n = 5$ droplets per solution).

The contact angle was estimated using Image J software to calculate the contact angle of a droplet of lactate solution in HDEHP solution in PFA tubing. An estimate of 155° was obtained and used for predictions (Table S1).

Viscosities were assumed to be similar to that of the pure solvents: $\mu = 1 \text{ mPa s}$ for water (used for aqueous solutions) and $\mu = 1.383$ for dodecane at 25 $^{\circ}\text{C}$ (used for HDEHP solution, data from CRC Handbook 77th Edition).

Determining Lanthanide concentrations

Lanthanide concentrations were determined using ICP-MS (single or multiple nuclides) by Argonne National Laboratory's analytical chemistry laboratory staff using standard analytical procedures. The pH of the aqueous solutions was measured using an Orion 525A+ pH meter and Orion Ross 8272BN pH probe. The pH calibration was done using 4.01 and 7.00 buffer solutions, traceable to NIST.

Procedure and analysis method for kinetic experiments

Equilibrium concentrations ($C_{eq} = C_{eq(aq)}$ and $C_{eq(org)}$, [M]) were obtained off-device by vortexing the aqueous and organic solutions together overnight and performing ICP-MS analysis. This provided an independent measurement of $K_D = C_{eq(org)} / C_{eq(aq)}$,

Initial concentrations (C_0 , [M]) were measured via ICP-MS of the initial aqueous feed

The time of extraction was varied in a device with a length of reaction channel of 88 mm by varying the total inflow rate, while maintaining a 1:2 or 1:1 volumetric ratio (as noted in text) of organic to aqueous phases. Aliquots of the aqueous sample stream were collected for each time point and analyzed offline by ICP-MS.

The data was plotted as aqueous lanthanide concentration, C , vs. time. Data was fit according a first order decay equation for the equilibrium $C \leftrightarrow C_{org}$, with forward and backward rate constants given by k_{ao} and k_{oa} , respectively, equilibrium constant $K_D = k_{ao}/k_{oa} = C_{org,eq}/C_{eq}$, and initial aqueous concentration C_0 . Assuming that $C_{org} = 0$ initially and that there are no side reactions to consume the aqueous metal ion, the rate equation is $dC/dt = (A/V) (k_{oa} C_{org} - k_{ao} C)$. Integration from $t = 0$ to t and $C = C_0$ to C gives ^{2,3}

$$\frac{C_{eq} - C}{C_{eq} - C_0} = e^{-k_{oa} (A/V)(1+(V_{org}/V_{aq})K_D)t}$$

Where

C = aqueous concentration [M]

C_{eq} = concentration at equilibrium [M]

C_0 = initial concentration [M]

A = interfacial area [mm²]

V = volume of each phase [mm³]

All parameters except k_{oa} [mm/s] were known and were fixed during the fit. From the fitted k_{oa} and known K_D , we solved for the forward rate constant $k_{ao} = k_{oa} K_D$ [mm/s].

Analytical prediction of mixing time in microfluidic droplets

Analytical predictions of the mixing time were made for droplets moving through straight microfluidic channels at a volumetric flow rate Q [m³/s] by following the method of Burns.⁴ First, the Peclet number Pe^* was calculated:

$$Pe^* = 4R^2 V / (D L),$$

$$\text{where } V = Q / (\pi R^2) \text{ [m/s]}$$

$$R = \text{radius of channel} = 63 \text{ } \mu\text{m}$$

$$D = \text{diffusion coefficient of solute} = 5 \times 10^{-10} \text{ m}^2/\text{s}^5$$

$$L = \text{length of droplet} = 250 \text{ } \mu\text{m}$$

Pe^* was high (>100) for all flow rates used here (Table S2), indicating that mixing was dominated by convection. Next, the predicted time to 90% mixing, t_{mix} , was calculated:

$$t_{mix} = (44.1 Pe^{*-2} + 0.286 Pe^{*-2/3}) (4R^2/D).$$

Predicted mixing times are reported in Table S2, and decreased by 25-fold as the total flow rate increased from 1 to 100 $\mu\text{L}/\text{min}$.

References:

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- (4) Rhee, M.; Burns, M. A. *Langmuir* **2008**, *24*, 590-601.
- (5) Danesi, P. R.; Vandegrift, G. F.; Horwitz, E. P.; Chiarizia, R. *J. Phys. Chem.* **1980**, *84*, 3582-3587.

Table S1. Device dimensions and fluid properties used to predict critical hole size for pure separation of aqueous and organic phases.

Fluid properties		
γ	7	mN/m
θ	155	deg
μ -org	1.383	mPa s
μ -aq	1	mPa s
Main tubing		
R1	63	μm
L1	112	mm
$L_{(\text{rxn channel})}$	88	mm
Withdrawal tubing		
R2	1181	μm
L2	200	mm

Table S2. Simulated and predicted mixing times as a function of flow rate

Q , $\mu\text{L}/\text{min}$	V , m/s	Calculated Pe^*	Predicted t_{mix} , s
100	0.13	1.7×10^4	0.014
10	0.013	1.7×10^3	0.064
1	0.0013	1.7×10^2	0.34

Complete References from main text:

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