Electronic Supplementary Material (ESI) for Lab on a Chip.

Time Capsule: An autonomous sensor and recorder based on diffusion-reaction

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Electronic Supplementary Information

Contents

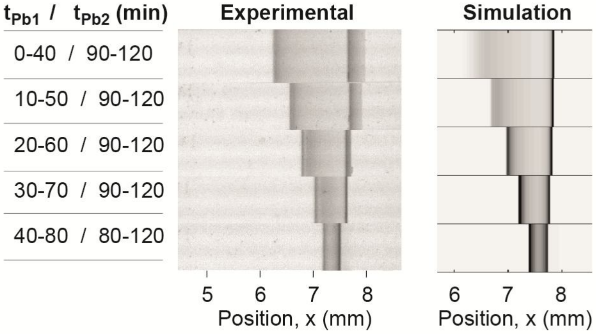
S1. Supplementary movie.

See separate file “S1_Supplementary_Movie_Figure2_formation.avi”.

This video visualizes the formation of precipitation bands shown in Figure 2a over time. The last frame in this video corresponds to Figure 2a in the main text. The concentration of $CrO_4^{2-}{}_{(aq)}$ in the reservoir was constant at 50 mM. It started diffusing into the channel at $t = 0$. The timer in the video (in red) ran continuously from 0 to 120 minutes. Seven independent 10-mm channels were exposed to 10 mM $Pb^{2+}{}_{(aq)}$ at different times. The green label “added” appeared in the video at t_{Pb} when $Pb^{2+}{}_{(aq)}$ was added to the system. The times that the seven channels are exposed to lead are thus: {0-120min, 10-120min, 20-120min, 30-120min, 40-120min, 50-120min, 60-120min} respectively.

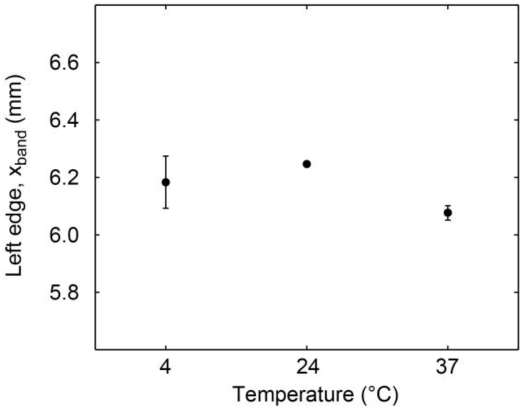
S2. Multiple exposures

Fig. S2. The device was exposed to Pb^{2+} twice. The first exposure was at variable time (t_{Pb1}), followed by a second exposure at a fixed time (t_{Pb2}). Simulation in COMSOL matched experimental results with a 2-4 % deviation.



S3. Dependence of band position on temperature.

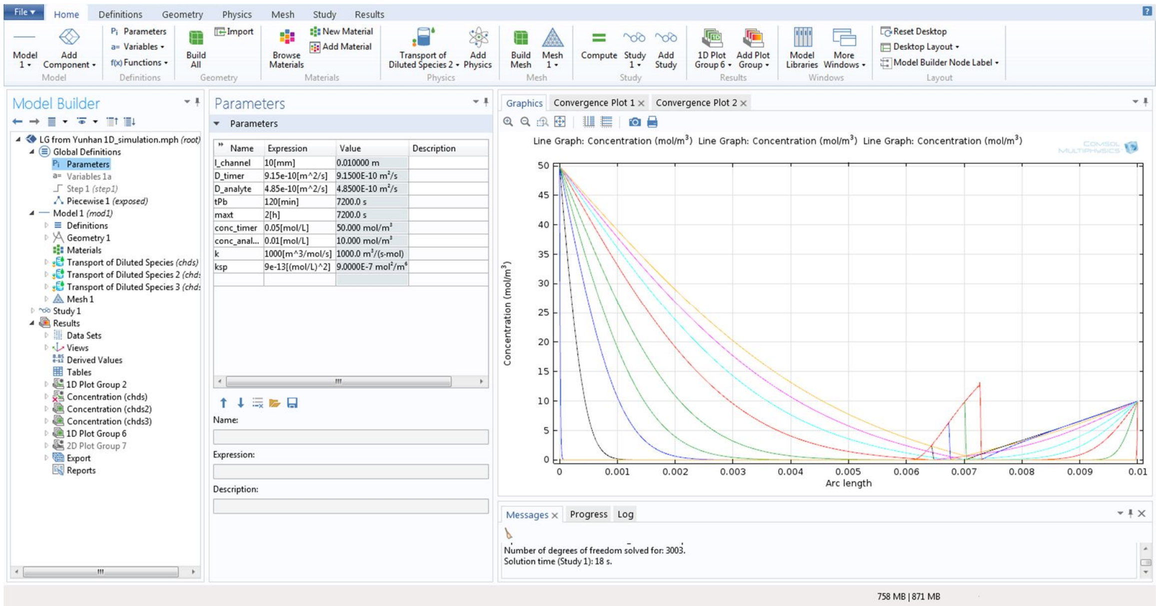
Fig. S3. Plots of left edge band positions at three different temperatures in a 10-mm channel where lead was introduced at t_{Pb} = 0 min. The positions were recorded at t = 2 hours. All other experimental parameters were the same as previous experiments.



S4. COMSOL simulation details.

We used the Transport of Diluted Species module in COMSOL Multiphysics 4.4. A linear, one-dimensional geometry (length = 10 mm) was used as the channel containing porous substrate. *Parameters for the timer reactant (c1):* Diffusion coefficient: D_{TR} = 9.15e-10 m^2/s; Reaction: -k*(c1*c2-ksp); Boundary concentration: c_{TR}^0 = 50 mM; Initial concentration in channel = 0. *Parameters for analyte (c2):* Diffusion coefficient: D_A = 4.85e-10 m^2/s; Reaction: -k*(c1*c2-ksp); Boundary concentration: c_A^0 = 0 mM resp. 10 mM; Initial concentration in channel = 0. *Parameters for the precipitate*: No diffusion; Reaction: k*(c1*c2-ksp); Initial concentration in channel = 0. Other simulation parameters: k = 1,000 $m^3/mol/s$; K_{sp} = 9e-13 mol^2/l^2.

Fig. S4. Screenshot from COMSOL Multiphysics' user interface showing the simulation used to generate the concentration profiles discussed in the main text and shown in Fig. 1b.



Parameters

Name	Expression	Value	Description
l_channel	10[mm]	0.010000 m	
D_timer	9.15e-10[m^2/s]	9.1500E-10 m²/s	
D_analyte	4.85e-10[m^2/s]	4.8500E-10 m²/s	
tPb	120[min]	7200.0 s	
maxt	2[h]	7200.0 s	
conc_timer	0.05[mol/L]	50.000 mol/m³	
conc_anal...	0.01[mol/L]	10.000 mol/m³	
k	1000[m^3/mol/s]	1000.0 m³/(s·mol)	
ksp	9e-13[(mol/L)^2]	9.0000E-7 mol²/m⁶	

Name:

Expression:

Description:

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Number of degrees of freedom solved for: 3003.
Solution time (Study 1): 18 s.
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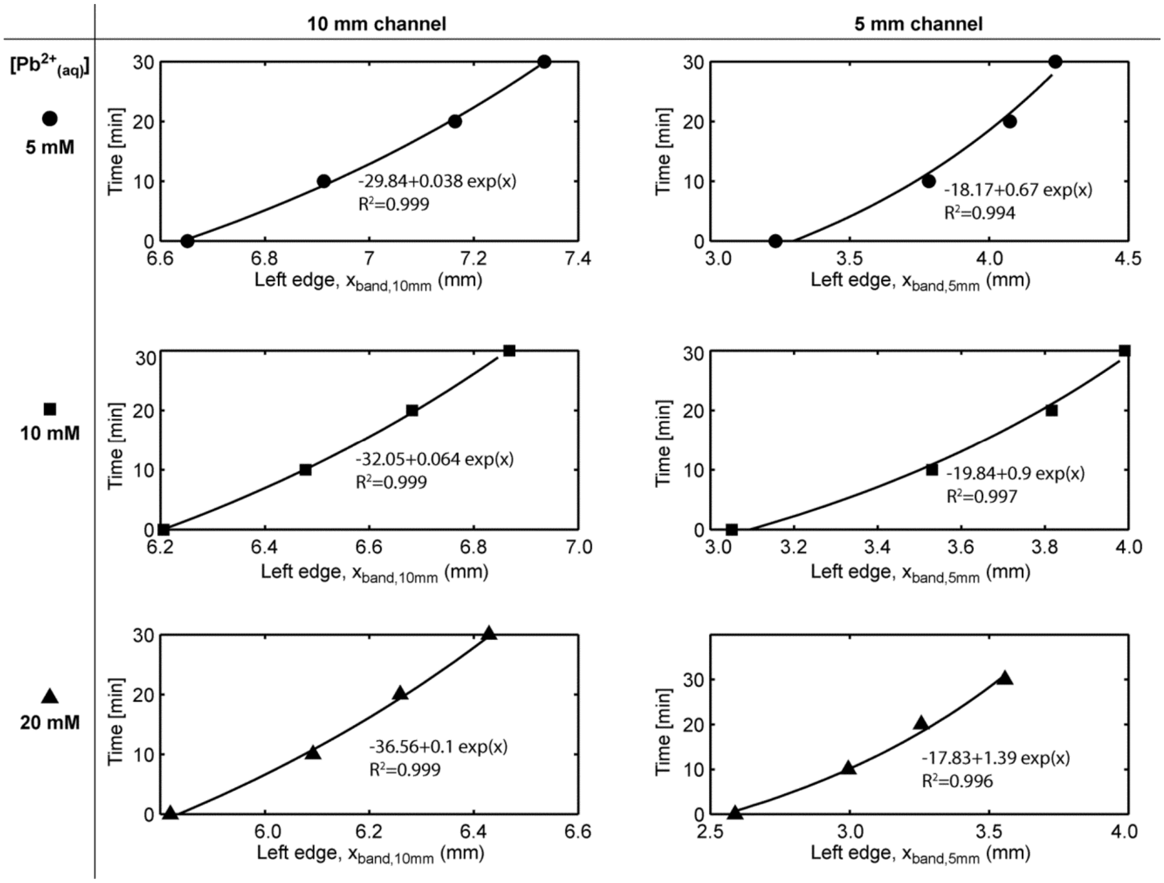
S5. Fabrication details.

For most characterization experiments, we used standard photolithography to fabricate the mold for the microchannels (width × height = 1 mm × 30 μm). Poly(dimethylsiloxane) (PDMS) was cured around this mold and bonded to a glass slide after the two reservoirs for timer reactant and analyte were made with a hole puncher (diameter 4 mm, height 7 mm). These reservoirs were not sealed at the top, and facilitated the exchange of solutions. To form the porous substrate, we injected 0.5 % agar at 80 °C into the channel. The agar gelled upon cooling to room temperature. The prototype shown in figure 1c was constructed by bonding two PDMS parts. The bottom part was a solid, flat (1 mm thin) piece of PDMS. The top part contained two channels (of lengths 5 mm and 10 mm respectively), and a reservoir for the timer reactant. The mold of the channels was made by lasing-cutting a double-sided tape, and the mold of the time reactant reservoir was made from an acrylic block placed on top of the tape. The entire device was filled with 0.5 % agar at 80 °C. The gel in the reservoir was removed using a syringe and needle before gelation occurred. After gelation completed inside the channels, the reservoir was filled with timer reactant using another syringe and needle. In this paper, we used the channels immediately after the timer reactant was injected. Future work will include methods to trigger the diffusion of the timer reactant.

S6. Curve fitting to experimental data.

Fig. S5. Plots of the left edge positions of precipitation bands x_{band} as a function of t_{Pb} for 10 mm and 5 mm channel lengths and for three analyte concentrations (5, 10, 20 mM). The curves are fits to data with the equations and R^2 goodness-of-fit indicated on the plot.



S7. Precipitation band formation.

The precipitation band profile can be predicted qualitatively based on the instantaneous local concentration gradient of the timer reactant and analyte respectively. We identify three scenarios to demonstrate how the band profile evolves with time in **Figure S6**:

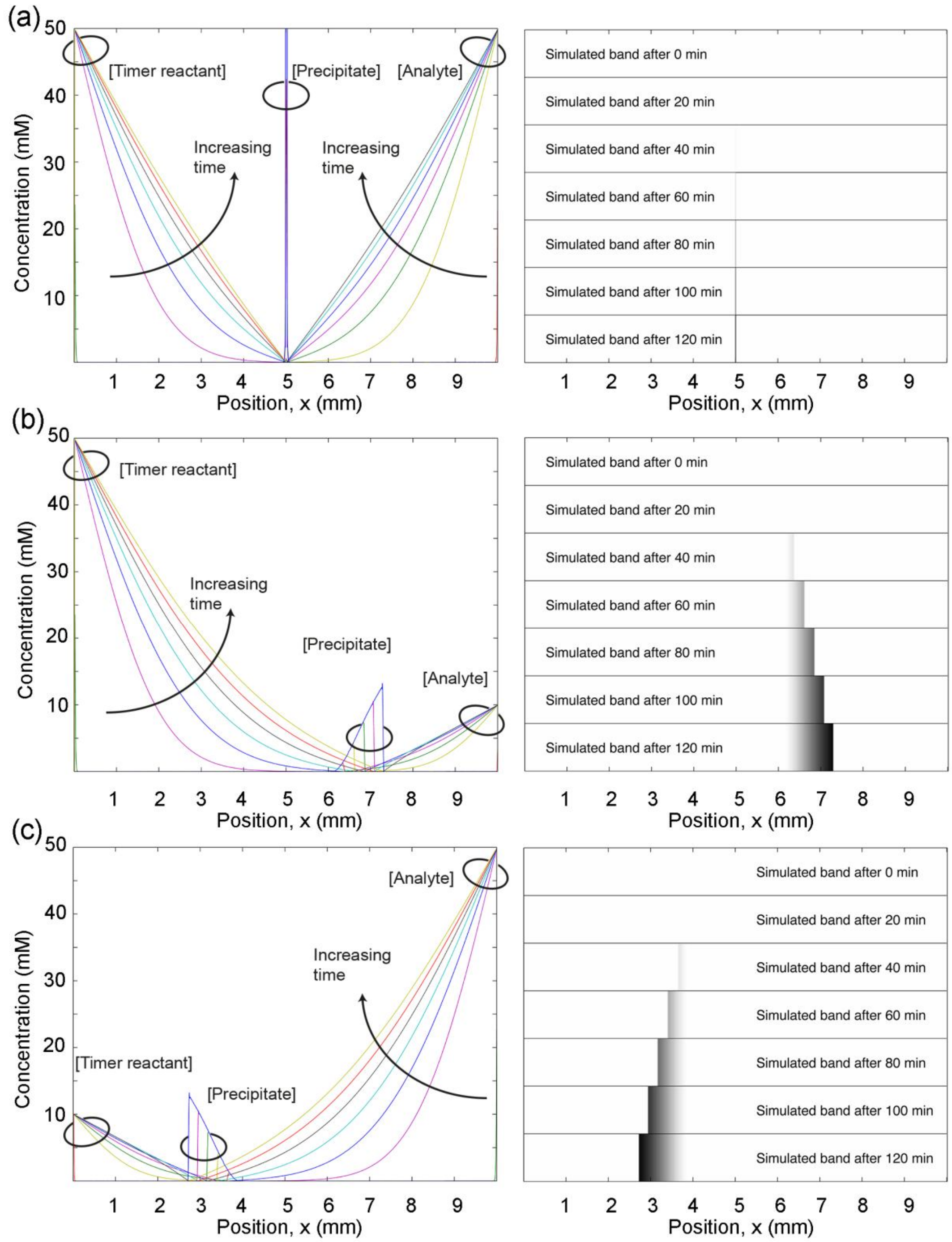
(a) $|dc_A/dx| = |dc_B/dx|$ → The precipitation band stays at a fixed position and accumulates as a sharp peak. This condition can be obtained if, for example, the diffusion coefficients of the timer reactant (A) and the analyte (B) are equal ($D_A = D_B$) and their concentrations at the two ends of the porous substrate are equal ($c_A^0 = c_B^0$), for reaction order of one for both the reactant and the analyte.

(b) $|dc_A/dx| > |dc_B/dx|$ → The precipitate concentration profile has a positive slope ($dc_{precipitate}/dx > 0$), which results in a darker right edge of the band. For this simulation: $D_A > D_B$ and $c_A^0 > c_B^0$.

(c) $|dc_A/dx| < |dc_B/dx|$ → The precipitate concentration profile has a negative slope ($dc_{precipitate}/dx < 0$), which results in darker left edge of the band. For this simulation: $D_A < D_B$ and $c_A^0 < c_B^0$. Although the left edge of the precipitation band shifts towards the timer reactant over time, this shift does not affect our measurements which always take place at a fixed observation time point (e.g., $t = 120$ min).

The integrated intensity of the precipitation band is proportional to the amount of precipitation product and scales with the duration of reaction and the concentration of the analyte (for a fixed concentration of timer reactant).

Fig. S6. COMSOL simulations of three scenarios resulting in different time evolution of the precipitation band profiles. Different colors of the curves represent concentration profiles at different time points. Note that in this figure, both the timer reactant and the analyte are introduced at time *t* = 0 for the total duration of the simulation.



S8. Pond water sample.

To show that the Time Capsule can work with non-ideal, non-pristine samples, we collected pond water on August 18, 2014 from the Hole 14 water hazard of the Stanford University Golf Course. The water was visually muddy. We replaced deionized water with this pond water, and spiked this water with lead nitrate to obtain a nominal $Pb^{2+}_{(aq)}$ concentration of 10 mM. We ran the same experiment as we did in the main text in Figure 2 for $t_{Pb} = 0$ using a 10-mm long channel. **Figure S7** shows that the band position obtained after t = 2 hours using this pond water closely matched that when lead was dissolved in deionized water. The slight difference in band position was likely due to the fact that the actual lead ion concentration was not at 10 mM. We suspect there were anions in the pond water that reacted with small amounts of lead we added, and resulted in a final concentration of lead that is slightly lower than 10 mM.

Fig. S7. Replacing deionized water with pond water gave similar results.