ELECTRONIC SUPPLEMENTARY INFORMATION (E.S.I.)

Recording Temporal Characteristics of Convection Currents by Continuous and Segmented-Flow Sampling

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ADDITIONAL TABLE

Table S1. Measurement of flow rate in the system depicted in Fig. 4A and S3 by weighing aliquots of water eluted from the flow line (Tygon tubing ID 0.13 mm). Preset flow rate: 30 µL min^{-1}. Sample collection time: 10 min.

	Sample mass / g		
Replicate No	**MS on**	**MS off**	**No ESI emitter**
1	0.229	0.271	0.294
2	0.230	0.242	0.293
3	0.228	0.274	0.300
Average	0.229	0.262	0.296
Flow rate at the outlet of the Tygon tubing (µL min^{-1})	22.9	26.2	29.6
Flow rate at the ESI emitter (µL min^{-1})	6.7 (29.6 – 22.9)	3.4 (29.6 – 26.2)	N/A

ADDITIONAL FIGURES

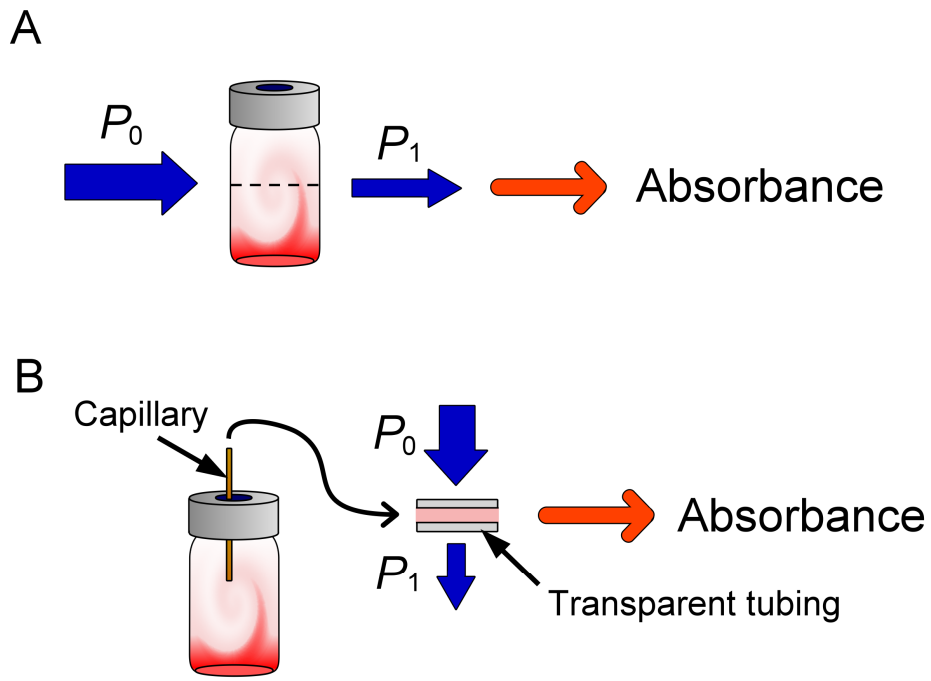

Fig. S1 An illustration of the absorbance detection of a non-homogeneous sample. (A) Direct measurement, which provides an "average" absorbance that does not reflect absorbance values at most points along the optical pathlength (dashed line). (B) An alternative sampling strategy: a small volume of the mixture is aspirated into a capillary, and transferred to the downstream absorbance detector. Symbols: P_0 – incident light; P_1 – transmitted light.

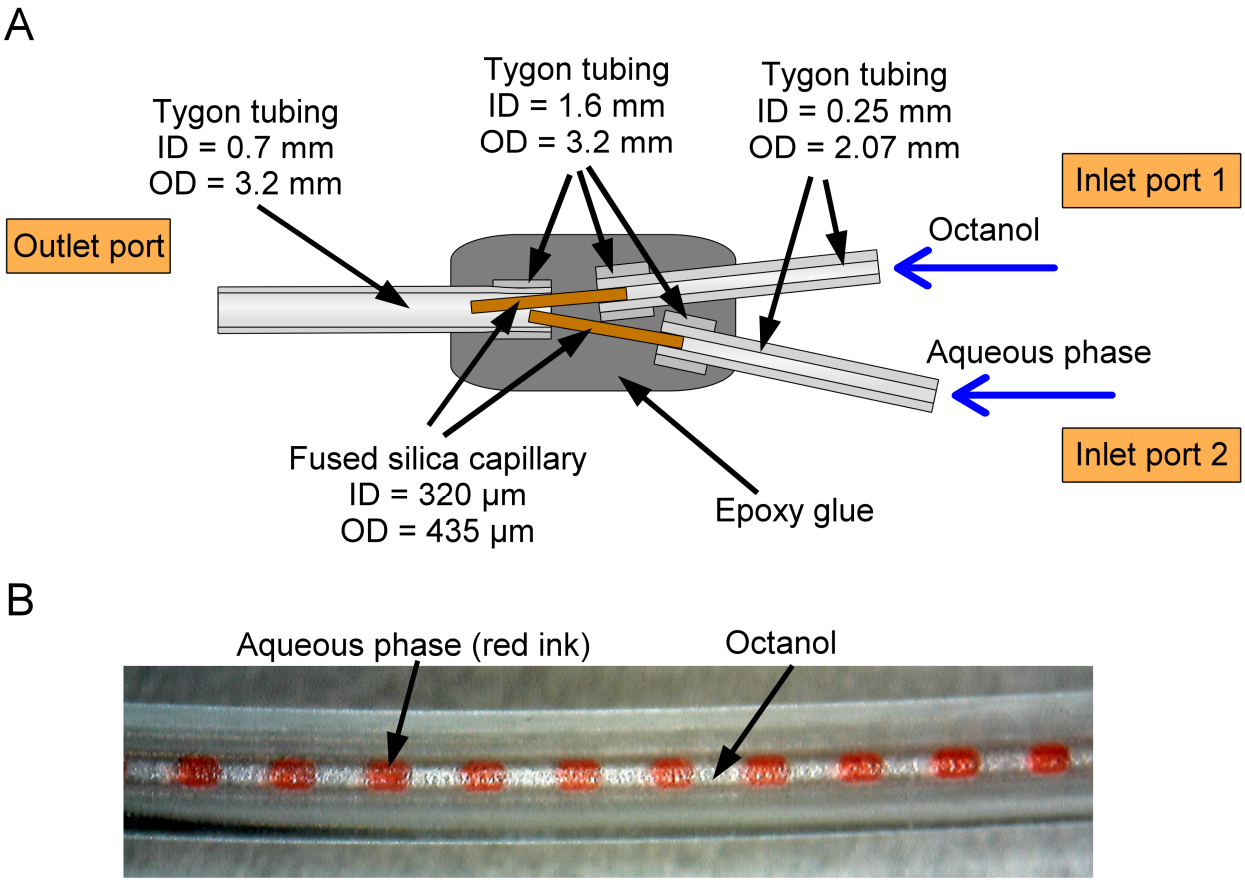

Fig. S2 A segmented flow generator. (A) The design of the Y-junction used to generate segmented flow. (B) Photograph of the segmented flow generated in the Y-junction. An aqueous solution of red ink and *n*-octanol were used as the immiscible phases.

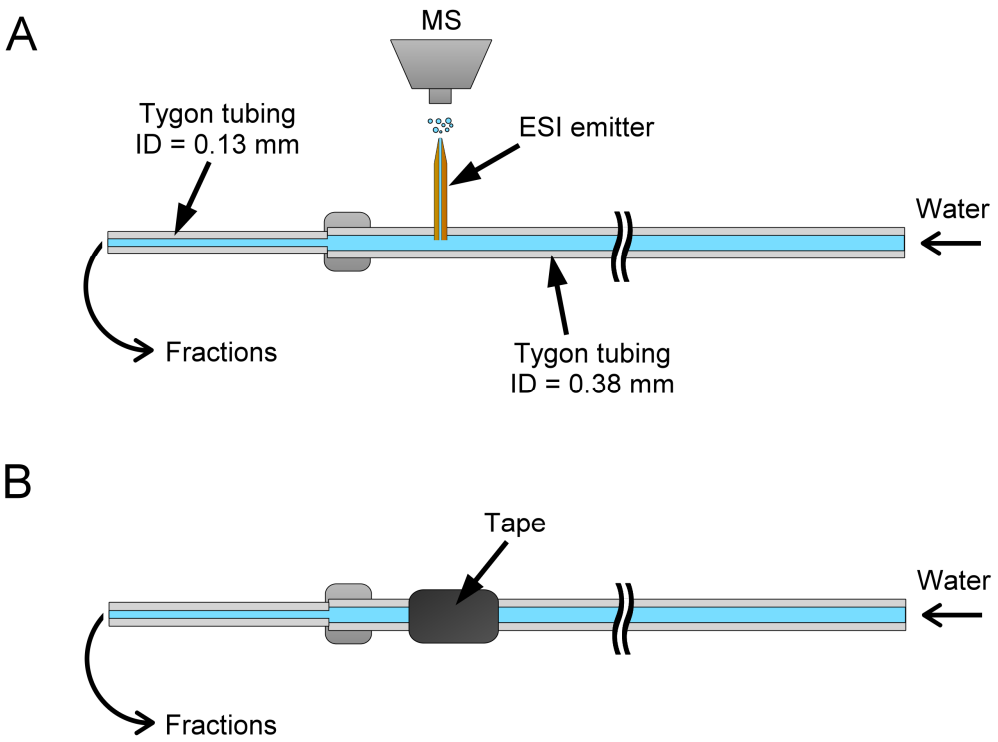

Fig. S3 Measurement of the effective flow rate in the fused silica capillary used as ESI emitter. (A) The ESI emitter is installed in the flow line, and the MS is turned on. (B) The ESI emitter is removed, and adhesive tape is used to prevent leakage of the liquid medium through the small hole made on the wall of the Tygon tubing.

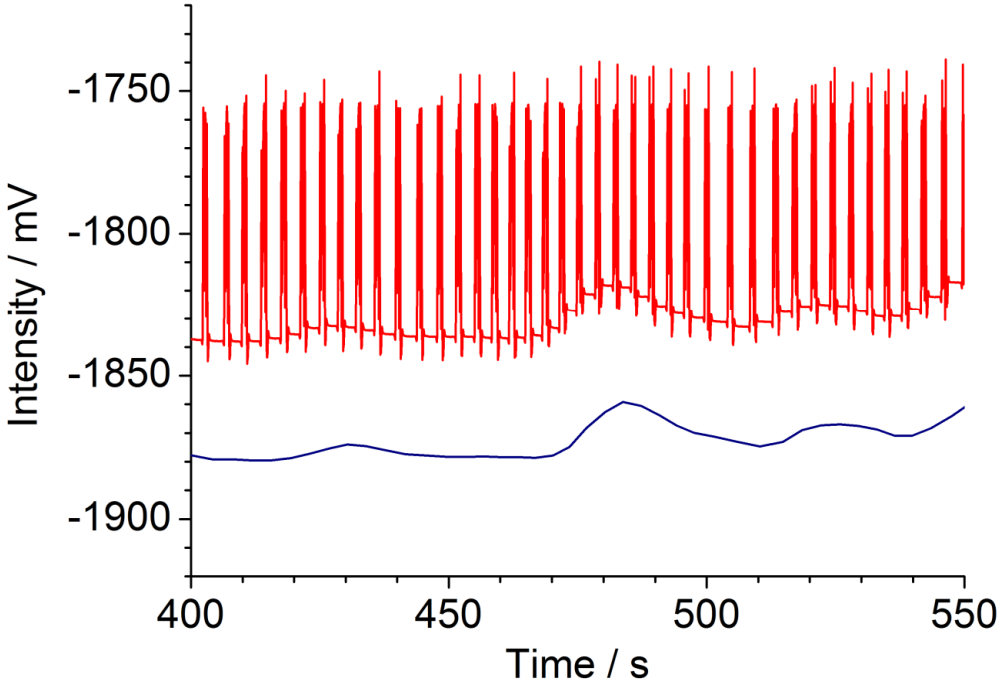

Fig. S4 Convective mixing of ferroin with water followed by segmented flow and flow-through optical detector (*cf.* Fig. 1; wavelength: 518 nm). The red line represents original data while the blue line shows the final data extracted by the custom software. The two traces were shifted vertically for clarity. The width of the signal corresponding to the aqueous plug (valley in the red trace) is ~ 4 s.

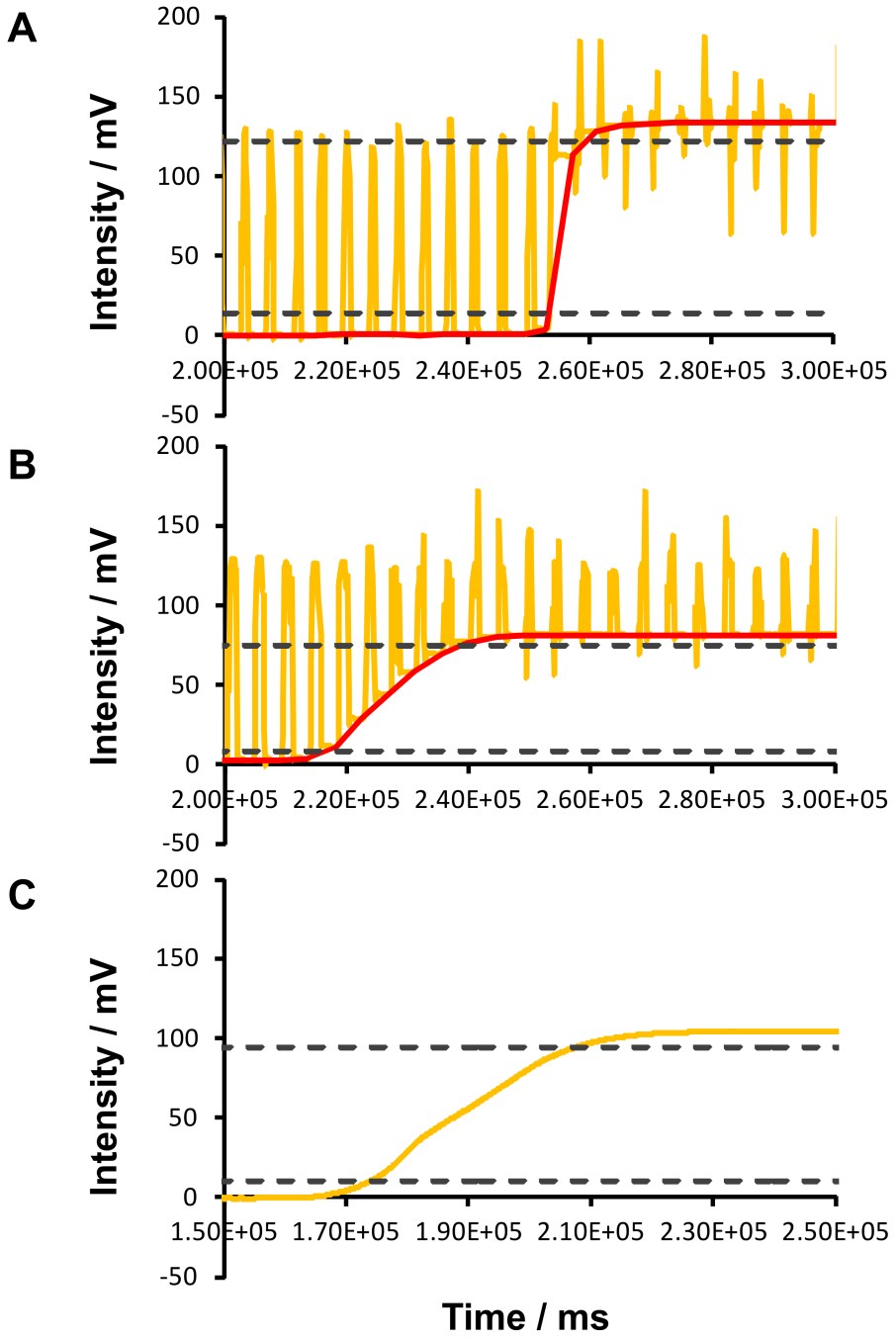

Fig. S5 Estimation of the temporal resolution. (A) Segmented flow sampling with switching vials (a vial containing pure water was quickly replaced with a vial containing a solution of ferroin). Rise time: ~ 8 s. (B) Segmented flow sampling with stirring (accelerated mixing of ferroin using magnetic stirrer). Rise time: ~ 21 s. (C) Continuous flow sampling with stirring (accelerated mixing of ferroin using magnetic stirrer). Rise time: ~ 33 s. Traces were shifted for clarity. Yellow lines in all the graphs correspond to the raw data, while red lines in (A) and (B) represent the treated data (after the removal of *n*-octanol peaks). Dashed lines represent $0.1I_M$ and $0.9I_M$ levels (where I_M is the maximum intensity).

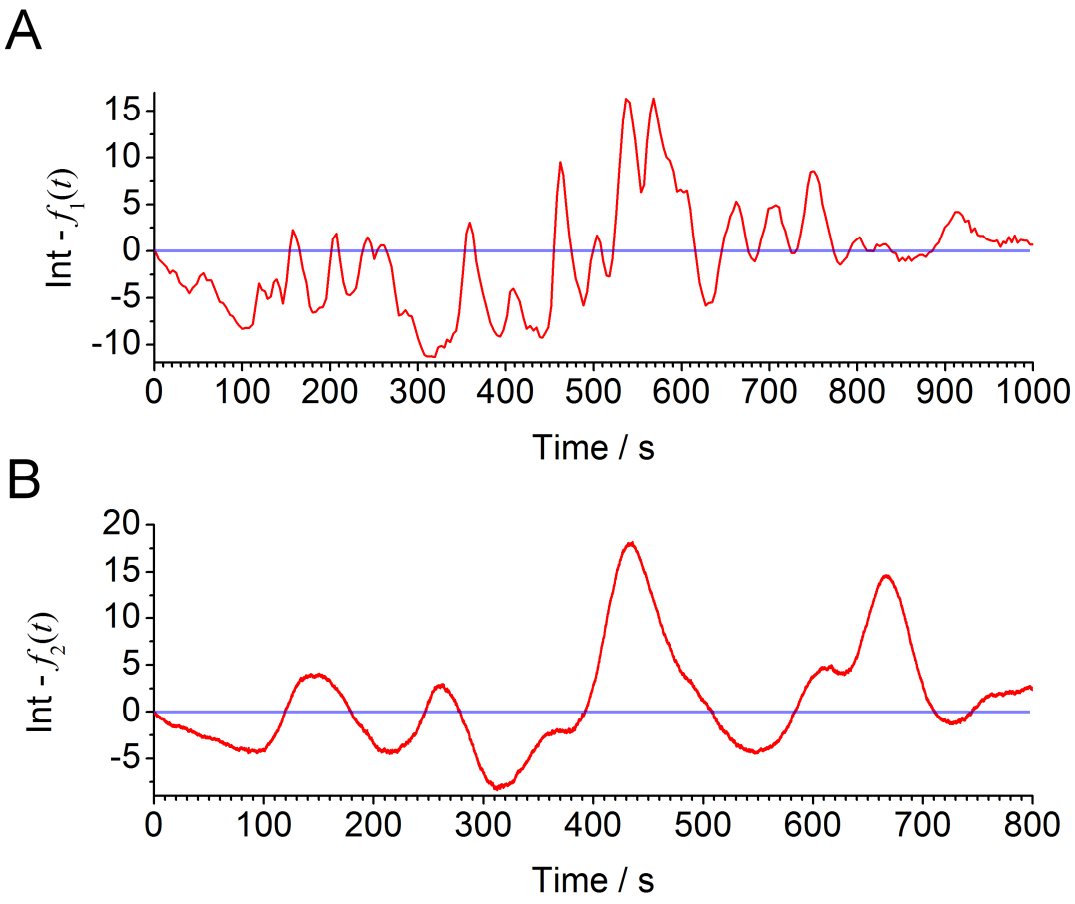

Fig. S6 An alternative representation of the data sets displayed in Fig. 2Ca and 2Da. The experimental data points were subtracted with the fitted exponential functions (A: $f_1(t) = 31 \times (1 - e^{(-0.0030x)})$; B: $f_2(t) = 27 \times (1 - e^{(-0.0030x)})$). Fluctuations of absorbance due to convection currents in the glass vial can be clearly seen.

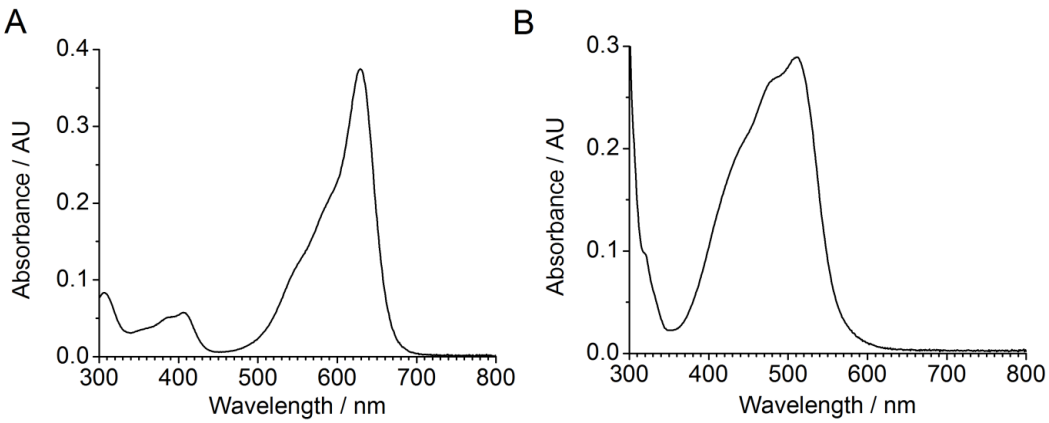

Fig. S7 UV/Vis absorption spectra of (A) ferroin (2.8×10^{-5} M), and (B) blue ink (1000× diluted original solution).

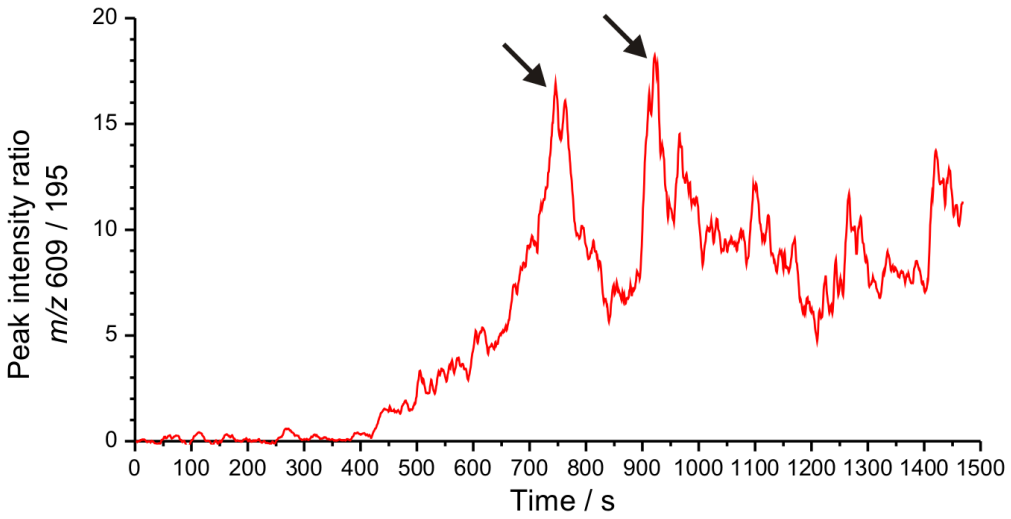

Fig. S8 Monitoring convection of reserpine ($[C_{33}H_{40}N_2O_9+H]^+$ at *m/z* 609) by ESI-MS in the presence of caffeine ($[C_8H_{10}N_4O_2+H]^+$ at *m/z* 195) used as an internal standard. The sample was: 220 µL 10^{-3} M reserpine in water. The convection medium contained 10^{-5} M caffeine dissolved in 25% ethanol. Exponential smoothing has been applied. Arrows indicate two distinctive fluctuations of reserpine concentration during the convection process.