Electronic Supplementary Material (ESI) for Reaction Chemistry & Engineering.

Supplementary Information

An improved liquid-liquid separator based on an optically monitored porous capillary

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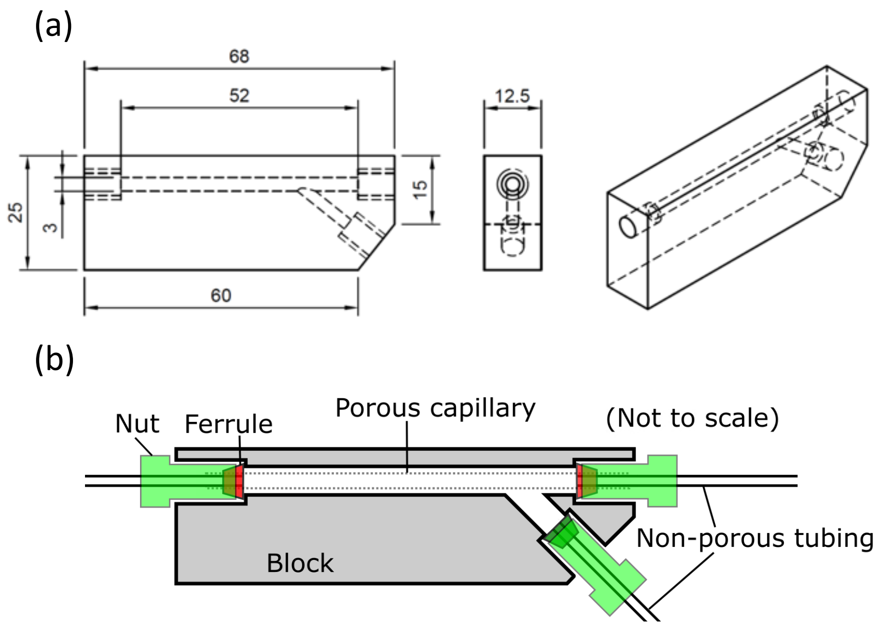

Fig. S1 – Design and assembly of the separation block (a) Technical drawing of separation block. Dimensions are in millimetres, and all threads are ¼”-28 UNF standard. The block is machined by hand from a single aluminium block, using a hacksaw to make the 45° angle of the side-channel port and a pillar drill for the holes. Each port is subsequently tapped with ¼”-28 (UNF) threads for connection of fluidic fittings. **(b)** Schematic showing fluidic connections to the separator block. The porous capillary is crimped to non-porous tubing at opposing ports using 2.5mm ID ferrules and corresponding nuts (see Assembly instructions below). The side-channel tubing is secured using a 2-mm-ID ferrule and nut.

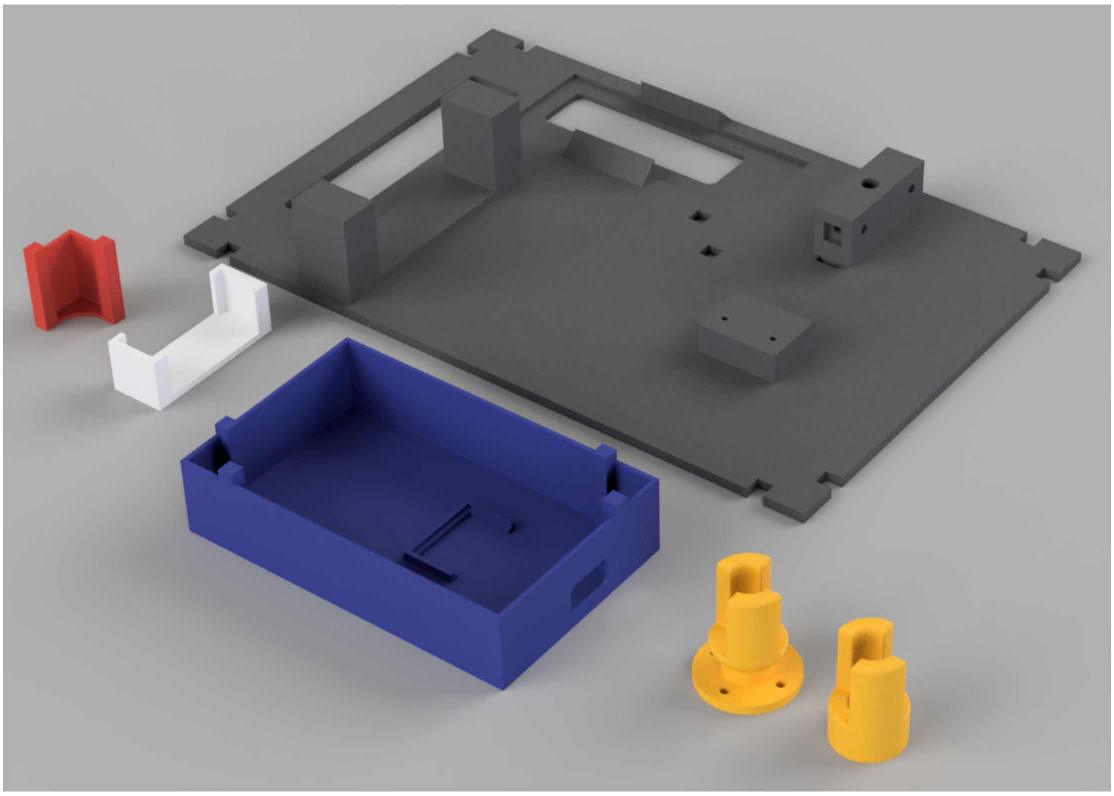

Fig. S2 – Rendered image of plastic parts used to assemble the separator. The separator parts are mounted on a common base-plate (grey). The separation block, motor and valve are mounted in fixtures on the top side of the base-plate. The electronic components, the microcontroller and (optional) battery, are housed in a box (blue) on the underside of the base-plate. A rectangular slot in the side of the box provides external access to the USB port of the microcontroller. The LED and the two light-to-frequency converters protrude into the sensor block via through-holes in the base plate. The LTF-converters are held in place by a tight-fitting “cap” (white) that fits around the sensor block, and the LED is held in place with a small dab of glue. A two-part spline coupling (yellow) is used to connect the positional servo motor and the needle valve. Three legs (red) slot into grooves in the corners of the base plate. One corner of the component box (blue) serves as the fourth “leg”.

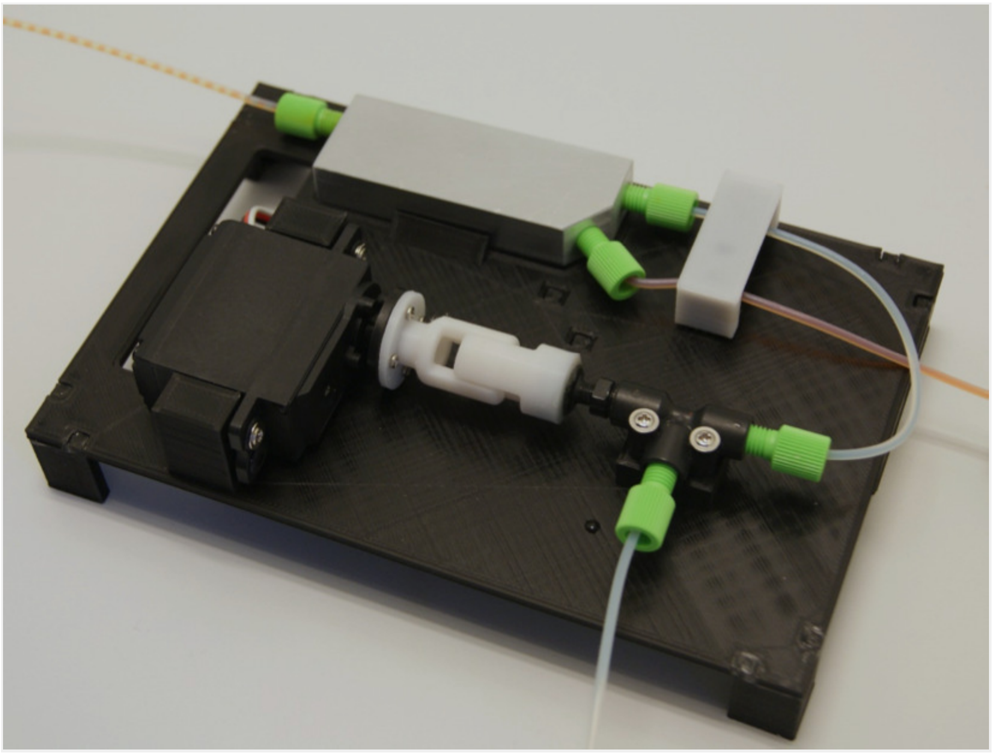

Fig. S3 – Photograph of assembled separator, showing separation block (silver, top left), sensor block (white, top right) and servo/valve assembly (bottom).

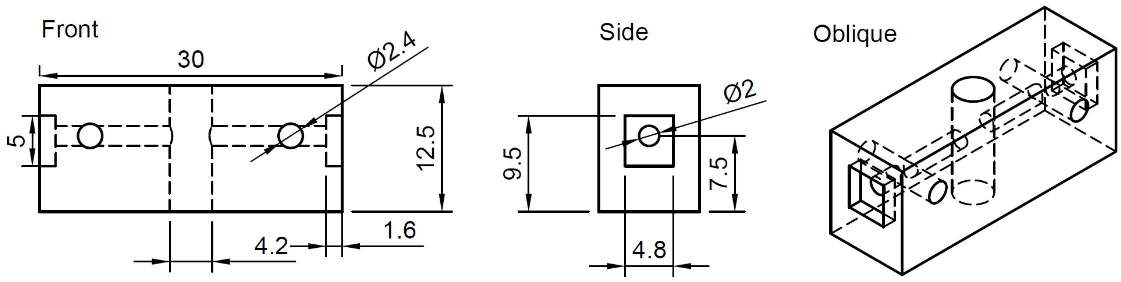

Fig. S4 – Technical drawing of sensor block, incorporating two parallel holes through which the outlet tubing from the T- and S- channels are separately threaded, plus a third orthogonal through-hole that allows light to pass through the two channels. A void in the centre of the block houses a light-emitting diode, while recesses on opposing faces of the sensor block house the two light-to-frequency converters. Dimensions are in millimetres.

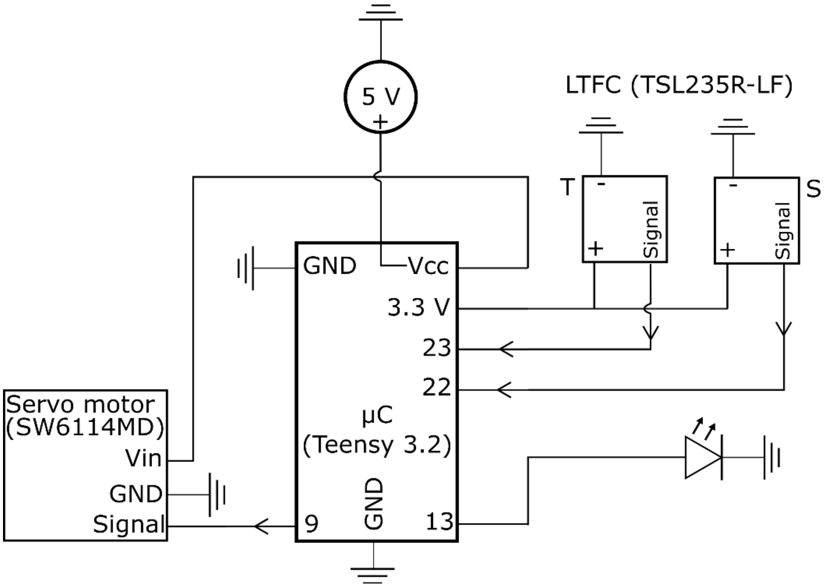

Fig. S5 – Circuit diagram for separator – The separator uses five discrete components: a microcontroller (here a Teensy 3.2), two light-to-frequency converters (LTFC, TSL235R-LF), a positional servo (King Max SW6114MD) and a visible or infra-red light-emitting diode (generic). The system may be powered using a battery, power supply or via the USB port of the microcontroller (μC). Owing to the simple design of the circuit, the Teensy 3.2 may be substituted by any microcontroller with three or more digital GPIO pins. The μC should preferably have one hardware PWM pin for pulse-width modulation control of the servo, but software PWM may be used if no hardware pin is available.

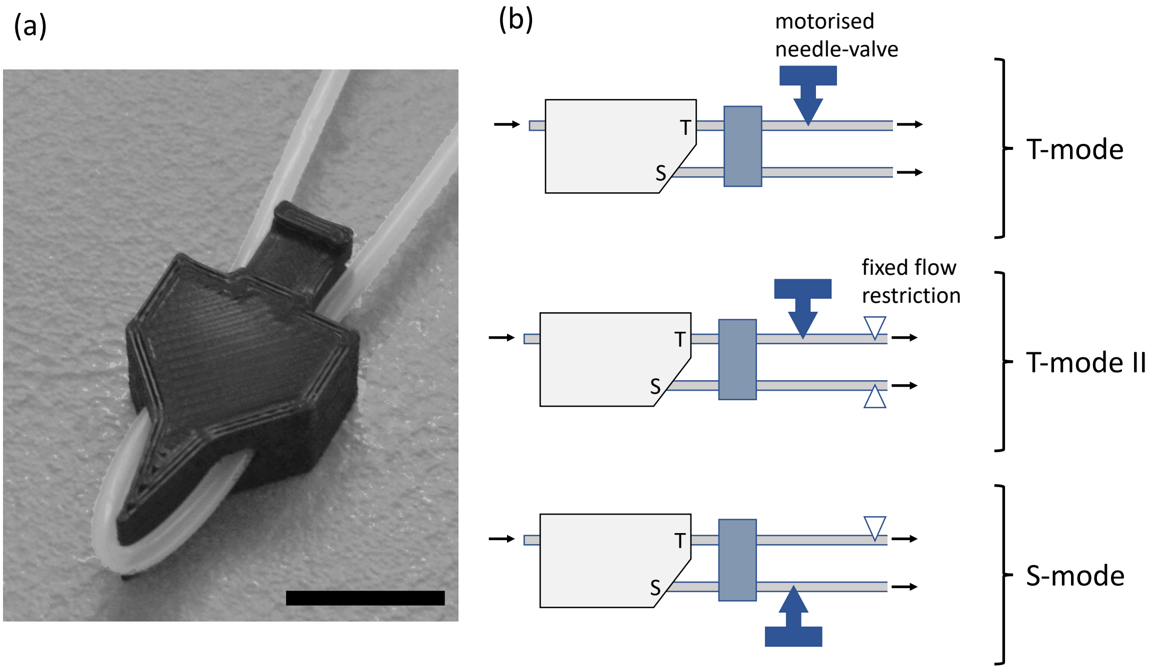

Fig. S6 – (a) Photograph of the fixed flow restriction used to induce high back pressure in an outlet channel. The plastic fitting enforces a 25° bend on the tubing, reducing its inner diameter. The scale bar denotes 1 cm. **(b)** Test configurations used for measurements reported in this paper. T-mode II shows the configuration used to obtain the transient data in Fig. 7b. All other measurements were carried out using the standard T- or S-mode configurations.

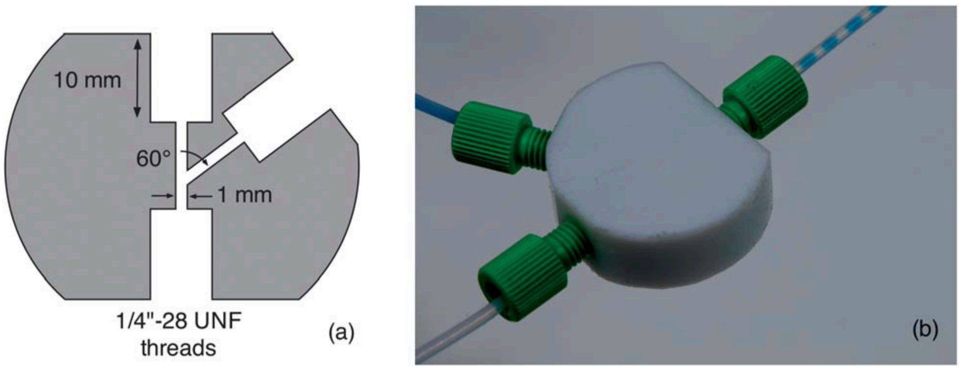

Fig. S7 – PTFE droplet generator: (a) schematic of channel architecture; **(b)** photograph of droplet generator in action, using equal flow-rates of water and PFPE. Taken from J. H. Bannock, T. W. Phillips, A. M. Nightingale and J. C. deMello, *Anal. Methods*, 2013, 5, 4991 - Published by The Royal Society of Chemistry.

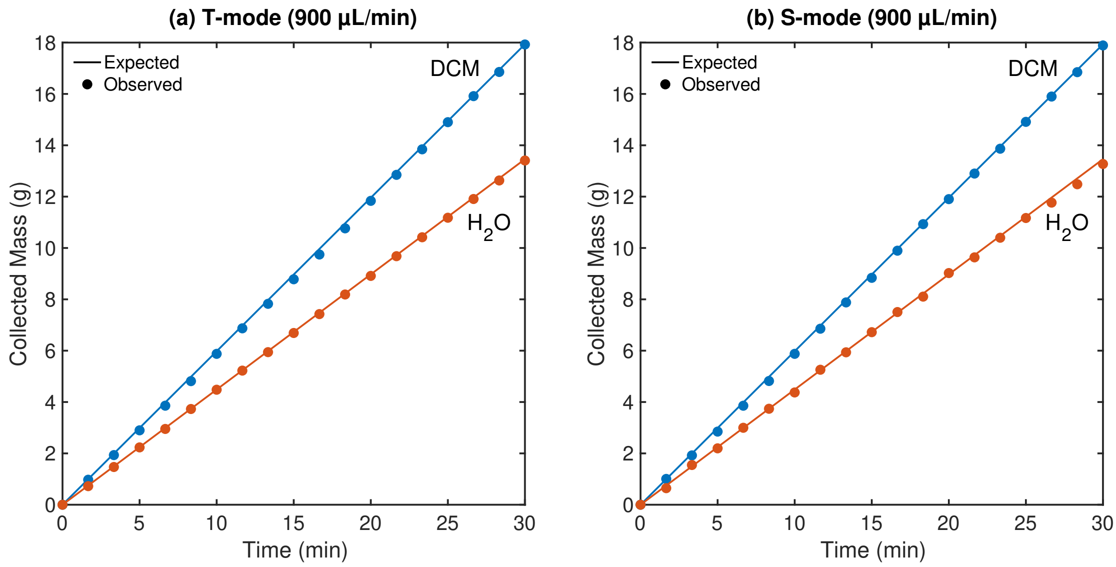

Fig. S8 – Throughput of automated separator. Graphs showing for T-mode **(a)** and S-mode **(b)** operation the masses of water and DCM collected at the outlets *versus* time, using equal injection rates of 450 μL/min. The masses were recorded at 100-s intervals *after* the separator had reached convergence. The circular markers denote experimental data, while the solid lines indicate ideal behaviour (assuming perfect separation and taking the densities of DCM and water to be 1.33 and 0.998 g/cm^3, respectively). Recovery rates were determined by fitting the experimental data to straight lines (with zero intercept) and comparing the extracted slopes to those of the ideal lines. In all cases the recovery was better than 99 %, with the slight shortfall from 100 % being attributable to evaporative losses, systematic inaccuracies in the syringe specifications or inaccuracies in the assumed densities.

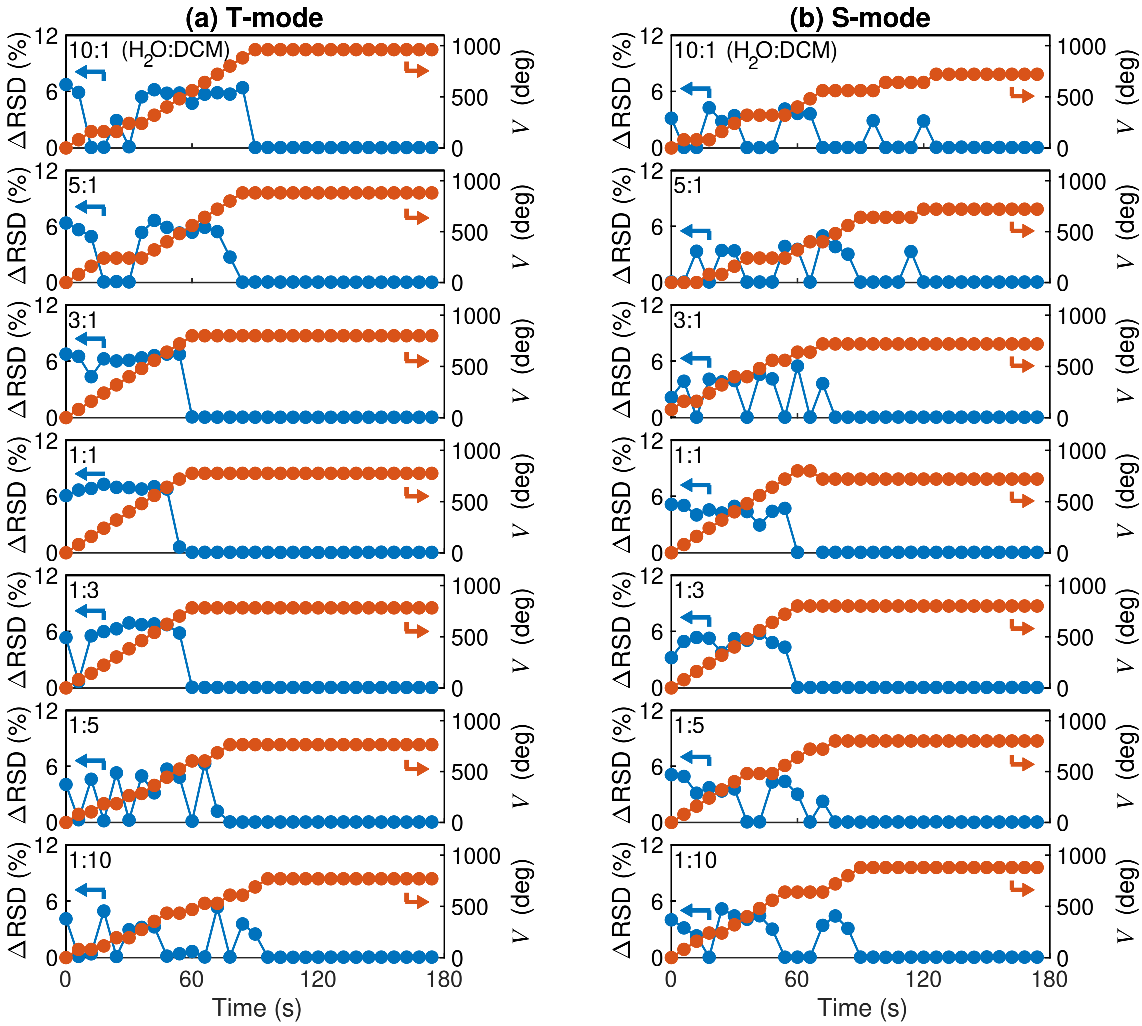

Fig. S9 – Performance of automated separator using imbalanced flow rates of water and DCM at a total flow rate of 1000 µL/min. Each plot shows for a different flow condition the valve position V (red line) and the differential RSD $\Delta\gamma$ (blue line) versus time, starting from an initial position of $V = 0°$. The left plots **(a)** show the T-mode behavior of the separator at H_2O:DCM flow-rate ratios in the range 1:10 to 10:1, with convergence to complete separation being achieved in 96 s or less. The right plots **(b)** show the equivalent S-mode behaviour, with convergence being achieved in 126 s or less.

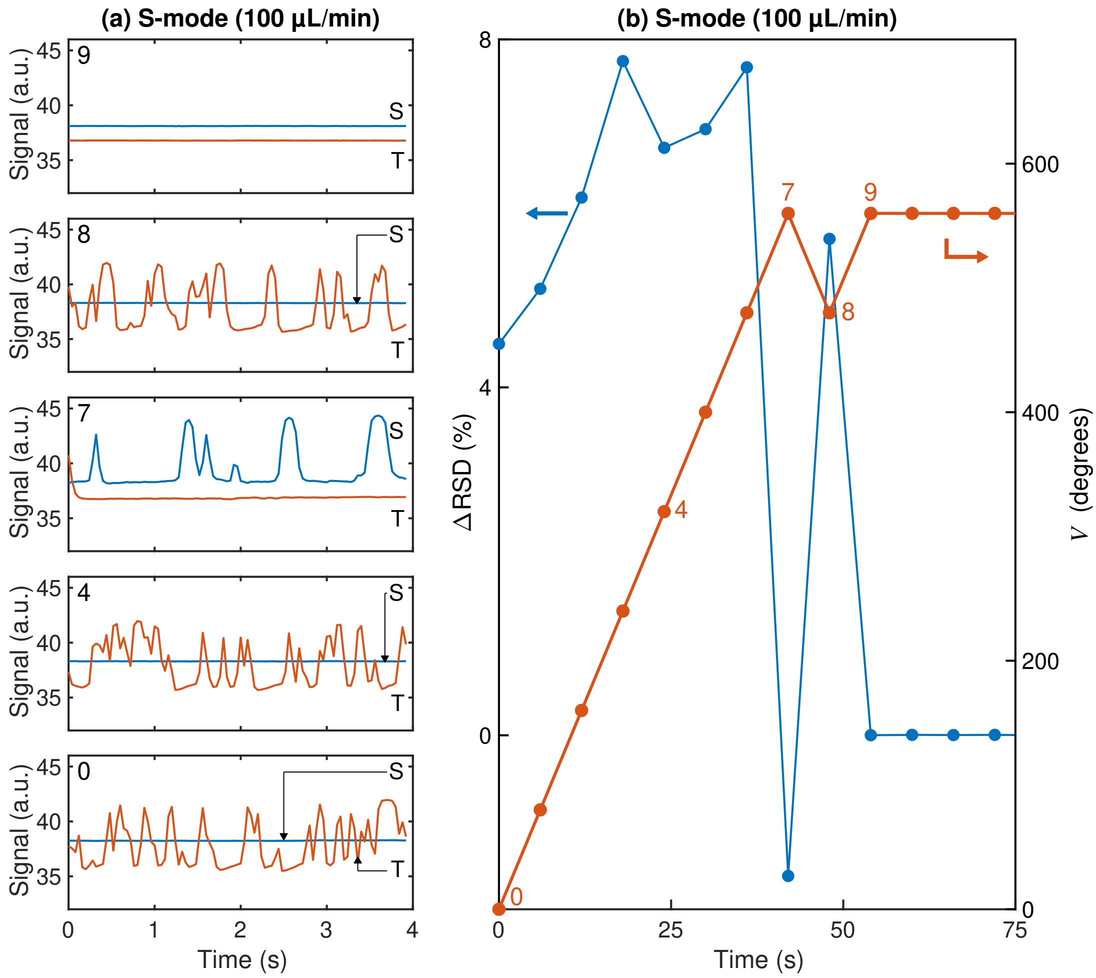

Fig. S10 – S-mode behaviour of automated separator, using equal flow rates of 50 µL/min for water and DCM. (a) Plots showing four-second traces recorded in the T-channel (red) and S-channel (blue) at key stages of the optimisation run. **(b)** Plot showing valve position V (red line) and differential RSD value $\Delta\gamma$ (blue line) versus time. Starting from an initial position of $V = 0°$, in which the entire two-phase fluid stream was forced through T, a series of seven large, positive $\Delta\gamma$ values of between four and eight percent were obtained due to strong fluctuations in the T-channel, causing the valve to make seven sequential positive adjustments at the maximum allowed adjustment of $\Delta V = +80°$. In iteration 7, the fluctuations switched from the T-channel to the S-channel, resulting in a negative differential RSD value of -1.6 % that caused a negative adjustment of $\Delta V = -80°$. In iteration 8, the fluctuations switched back to the S-channel, resulting in a large differential RSD of +5.7 % and a positive valve shift of $\Delta V = +80°$ that brought the separator into convergence. The brief appearance of fluctuations in the (active) S-channel at iteration 7 is attributable to the transient release of trapped fluid from the dead volume between the separator and the sensor block; this release occurs as soon as the valve is opened sufficiently to allow liquid flow in the active channel, and – as seen here – often results in a momentary change of valve direction.

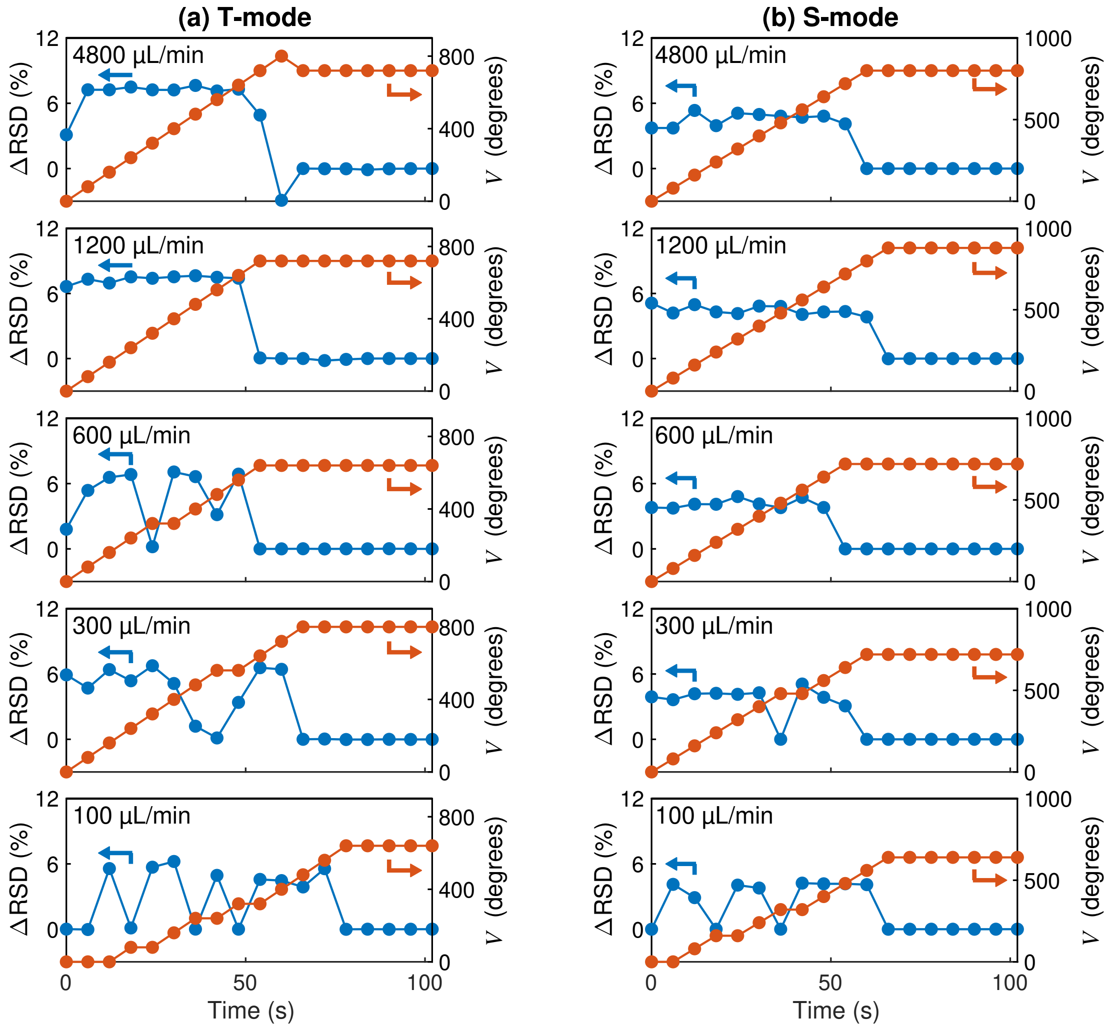

Fig. S11 – Performance of automated separator under various flow rates, using equal injection rates of water and hexane. Each plot shows for a different total flow rate the valve position V (red line) and the differential RSD $\Delta\gamma$ (blue line) versus time, starting from an initial position of $V = 0°$. The left **(a)** and right **(b)** plots show the behaviour of the separator in T- and S- mode operation, respectively. Convergence to a state of complete separation is achieved in 78 s or less.

Assembly instructions

Separator block: The microporous tubing is expanded PTFE formed by extruding PTFE under gas flow (Aeos ePTFE, inner diameter = 1.8 ± 0.05 mm, outer diameter = 2.5 ± 0.05 mm, and internodal distance = 15 – 25 µm). To assemble the separator block, a 60-mm length of the microporous tubing is mated at one end with an appropriate length of non-porous, 2-mm fluidic tubing. The resulting join is secured by a 2.5-mm-ID ferrule. The length of tubing is then threaded through the through-hole of the separator block, and the ferrule is secured at the inlet using a nut, crimping the tubes together in the process. The microporous tubing protruding from the T-channel outlet is then secured to a second length of non-porous tubing in a similar manner. Care should be taken to avoid twisting or damaging the tubing when fastening.

Printed Parts: The spline parts are 3D-printed from poly lactic acid (PLA, RS Pro, RS components) using a 0.06 mm layer thickness with 100 % in-fill. After printing, the spline halves are smoothed by exposure to chloroform vapour for 20 minutes. All other plastic parts are printed using a 0.2 mm layer thickness with 50 % in-fill and used without further processing.

Mounting of components on the baseplate: The servo motor is secured to its mounts using rubber grommets and two 2-mm self-tapping screws. The 3D-printed spline is fastened to the servo horn using four 1.5-mm screws. The other end of the spline coupling is glued to the adjustment knob of the needle valve, and the valve is screwed into the pre-printed holes on the base-plate using two 2-mm self-tapping screws. The servo-valve assembly should be mounted in the fully closed position before the glue cures to ensure proper alignment. The three 3D-printed legs are press-fitted into their mounts. The LED and optical sensors are soldered to short (50 mm) lengths of wire and pushed through their respective holes in the base-plate. The LED is secured by a drop of transparent epoxy resin, and the optical sensors are held in place by the retaining clip.

Electronics: The microcontroller (Teensy 3.2) is mounted in a compartment on the underside of the base-plate by a friction fitting. The signal pins from the T- and S-channel light-to-frequency converters (TSL235R-LF, Texas Instruments) are connected to pins 23 and 22 of the µC respectively, and they are powered via its 3.3 V source, see Fig. S5. The positive terminal of the LED is soldered to pin 13. The servo is powered at 5V via the input power pass-through pad on the microcontroller, and the signal wire is connected to pin 9.

Video S1 - Movie showing separator operating in T-mode with equal injection rates of DCM and water (at a total flow rate of 900 μL/min). The DCM has been dyed with sudan orange dye for easy visualisation of the droplet stream (~20 mg/ml). To enhance contrast a white PLA base-plate has been used and the movie is shown in grey-scale.

Data and source code repository – Video S1, data files, source code for the microcontroller firmware, and hardware design files may be found at the following location: https://github.com/ajharvie/separator

Troubleshooting Guide

Solutions to commonly encountered problems

	Problem	Possible cause	Solution
1	**Valve moves erratically**	Low total counts at optical sensors.	Check LED is correctly powered. Check LED is correctly mounted within sensor block. Check optical sensors are correctly powered and connected.
		Servo motor is underpowered.	Power supply must be capable of delivering correct voltage (4.6 - 6 V) and current (up to 1 A)
		Spurious optical signals.	Check sensors are correctly mounted.
		Air bubbles in fluid stream(s).	Check connections are tight. Wait for bubbles to clear.
2	**Valve does not move**	No counts from optical sensors.	Check sensors are connected and powered correctly.
		µC or servo motor not powered.	Check power connections.
		T- and S-channel sensors are connected to incorrect pins of microcontrollers.	Modify connections accordingly.
		Valve tries to tighten but is already fully closed. This error is signified by the LED flashing five times.	Check servo is configured to move in the correct direction.
3	**Valve position oscillates about separation window**	Proportionality constant α is too high	Reduce α.
		Max allowable adjustment $\Delta V_{\max}$ is too high.	Reduce $\Delta V_{\max}$.
		Wait time before data acquisition t_d is too short.	Increase t_d.
4	**Separator requires too many iterations to reach separation window**	Max allowable steps $\Delta V_{\max}$ is too low.	Increase $\Delta V_{\max}$.
		Proportionality constant α is too low for solvent system.	Increase α.
5	**System gets close to separation window but then stops adjusting.**	Threshold RSD γ_{min} is too high.	Reduce γ_{min}.
6	**Valve makes spurious adjustments after separation window is reached**	Threshold RSD γ_{min} is too low.	Increase γ_{min}.
7	**Segmented flow emitted by both outputs**	Internal porous tubing has split.	Replace porous tubing
		Valve position is oscillating about separation window.	See **3**.
8	**No flow at non-metered output**	Excessive back pressure at that output.	Switch valve to other channel.
		There is a blockage.	Remove blockage.

Parts List

Part	Approximate Cost (material cost)
Off-the-shelf parts	
Positional servo motor (King Max, SW6114MD)	£15
Micro-metering needle valve (IDEX Health & Science, P-445)	£50 (cheaper options available)
µC (Teensy 3.2 or other)	£20 (cheaper options available)
2 × LTFC (TSL235R-LF)	2 × £2
LED (generic)	£ 0.10
5 × nuts + ferrules (IDEX Health & Science, F-294, P-353, P-363R)	£5
Fabricated parts	
Separation block	£2
3D-printed parts	£2