Electronic Supplementary Material (ESI) for Analyst.

Electronic Supplementary Information

Hydrophobic/hydrophilic patterned surfaces for directed evaporative preconcentration

Ben Tucker,[a] Matthias Hermann, [a] Alexa Mainguy,[b] and Richard Oleschuk*[a]

Surface Hydrophobicity

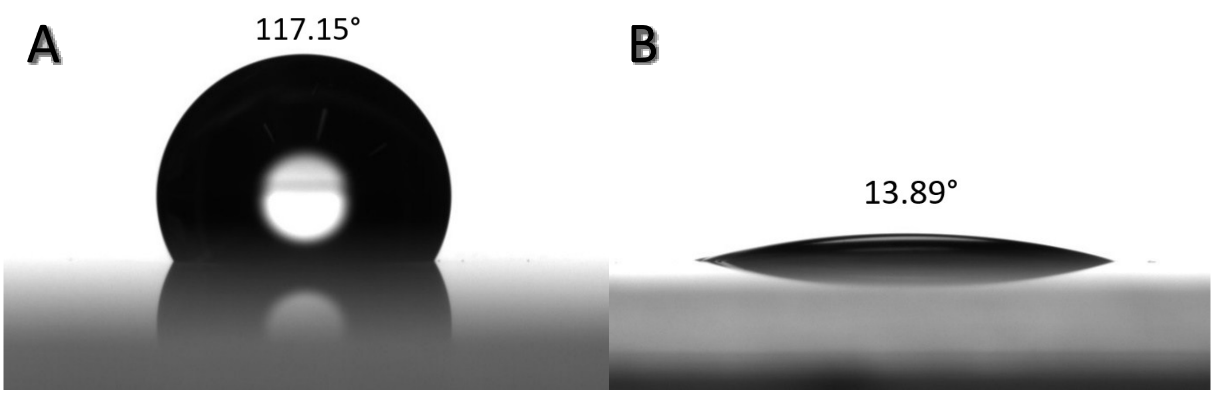


Figure S1: *Images taken on a Dataphysics OCA 15Pro contact angle measuring system depicting droplets (4μL) of water sitting on coated (A) and uncoated (B) glass slides.*

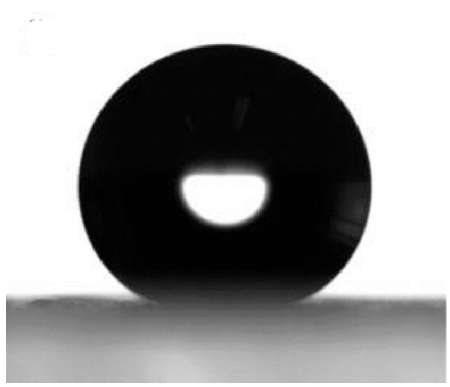


Figure S2: *A 5μL water droplet sitting on a UED-coated slide. WCA = 150° +/- 3°*

Mill-Broadening Zone

The mill-broadening zone (MBZ) is an area of additional hydrophilicity outside of the laser milling area. When deposited on SETs by discontinuous dewetting, droplets pin at this threshold of hydrophobicity/hydrophilicity. We calculate the MBZ as follows:

$$Wetting\ diameter = SET\ diameter + 2(MBZ)$$

$$MBZ = \frac{Wetting\ diameter - SET\ diameter}{2}$$

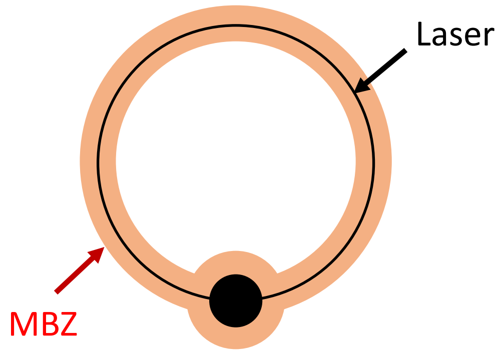


Figure S3: *Schematic of the MBZ resulting from laser ablation.*

SET Mill Depth Measurements

SET mill depth was characterized using a Bruker® ContourGT-K 3D Optical Microscope. Mill depth measurements were made for ring SETs made with higher laser powers (5, 7.5, 10mW). Measurements of SETs produced with lower laser power were unreliable as they were below the instrument capability.

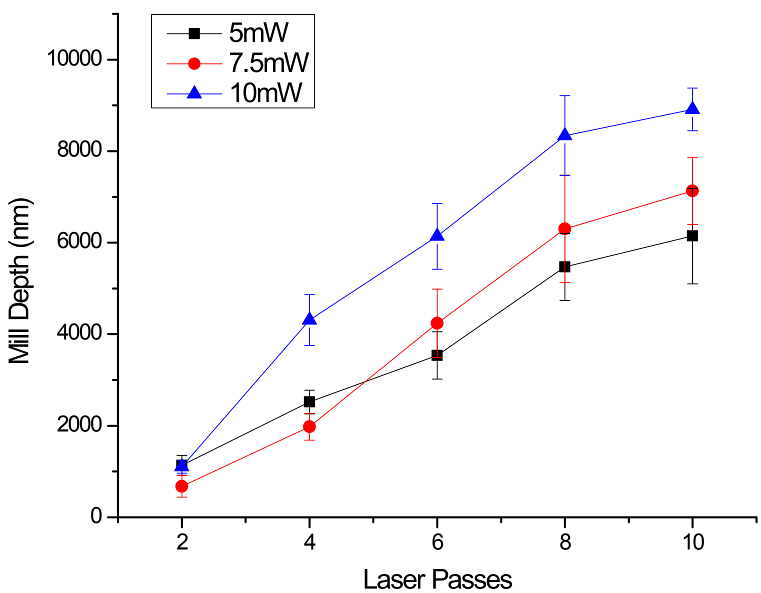


Figure S4: *Mill depth trend of ring-shaped SETs on Aculon-coated slides.*

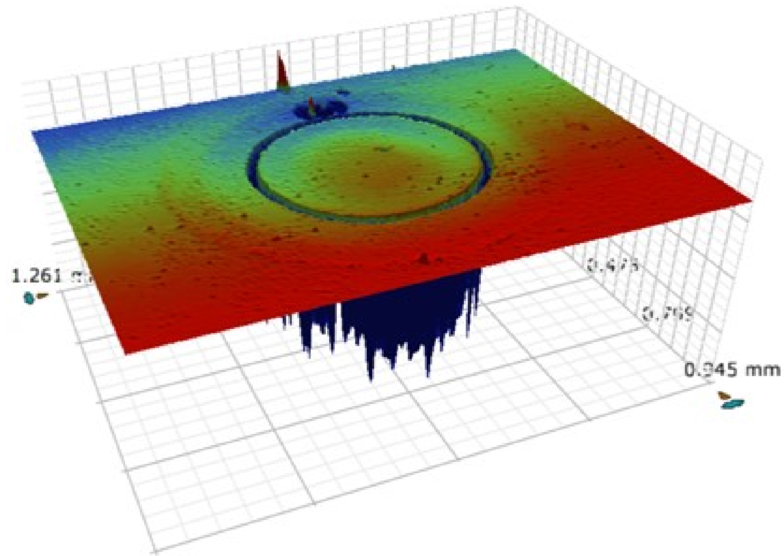


Figure S5*: Optical interference profilometer images of a ring-shaped SET (5mW, 8 passes). Captured using a Bruker® ContourGT-K 3D Optical Microscope. XY scale is 0.945mm x 1.261mm. Measured mill depth is 7772 +/- 395nm (n=3).*

The manufacturer states that the coating thickness of the adhesion promoter and hydrophobic coating are 5-100nm and 2-4nm, respectively. The optical microscope was unable to measure a difference between coated and uncoated regions of glass slides.

Effect of Laser Power

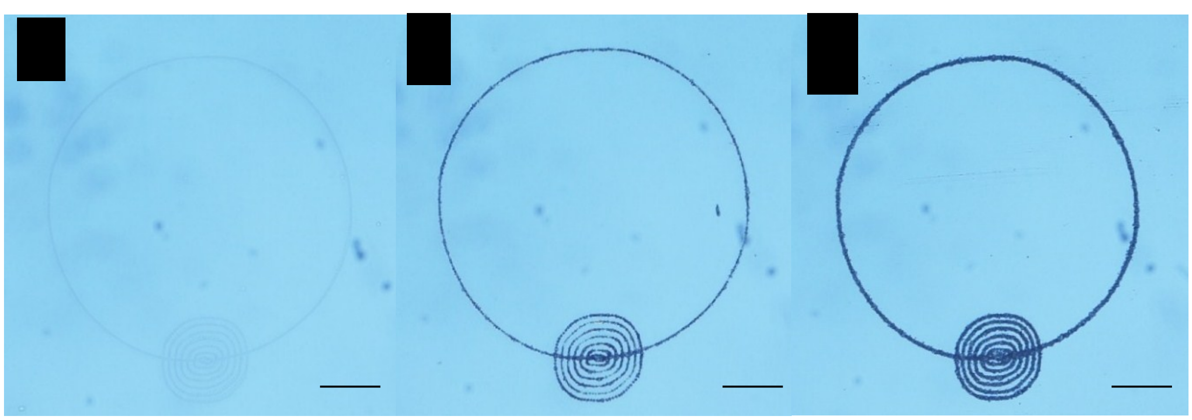
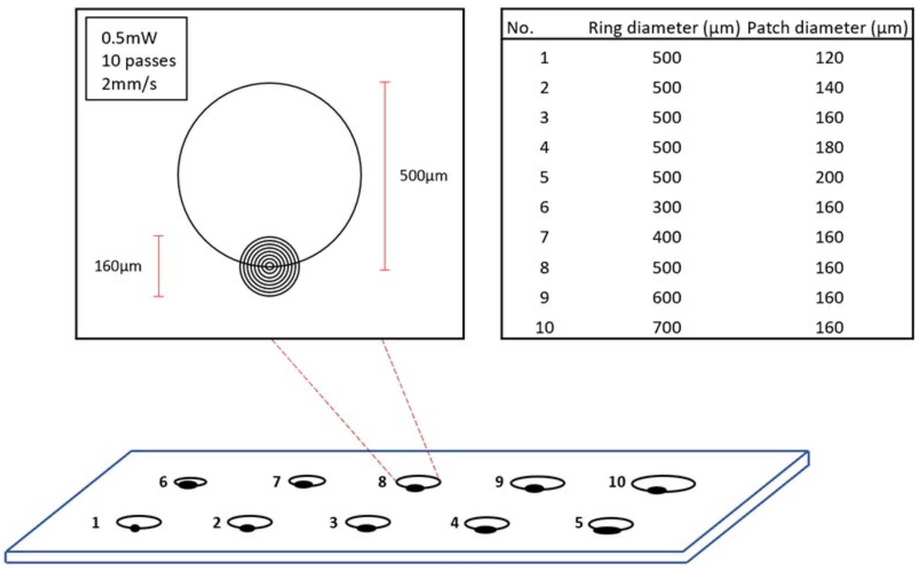


Figure S6*: Comparison of ring/patch SETs (500µm/140µm) milled at (A) 0.5mW, (B) 0.75mW, (C) 1.0mW. Scale bars are 100µm.*

SET Optimization Study

Figure S7 shows the chip fabricated for the parametric study of SET dimensions. SETs 1-5 have a ring diameter of 500 µm and patch diameters ranging from 120-200 µm. SETs 6-10 have ring diameters ranging from 300-700 µm and patch diameters of 160 µm. All SETs were fabricated at 0.5 mW and 10 laser passes.



No.	Ring diameter (µm)	Patch diameter (µm)
1	500	120
2	500	140
3	500	160
4	500	180
5	500	200
6	300	160
7	400	160
8	500	160
9	600	160
10	700	160

Figure S7: *Schematic of chip design for SET dimension optimization.*

Image Processing

Microscope images of droplet dried down on SETs were processed and measured for their RGB intensities in Image J. Greyscale histograms for the SET patch areas were collected (Fig. S8). Table S1 describes the image processing procedure in detail. Each greyscale value (A) was multiplied by its corresponding count (B). The average greyscale value of the background was determined and counts from 255 to the background value were set to zero to ensure the result corresponds to the SET patch area. The sum (channels 0-255) of A*B was divided by the sum of B to obtain a single greyscale value representing the average colour intensity of the given area.

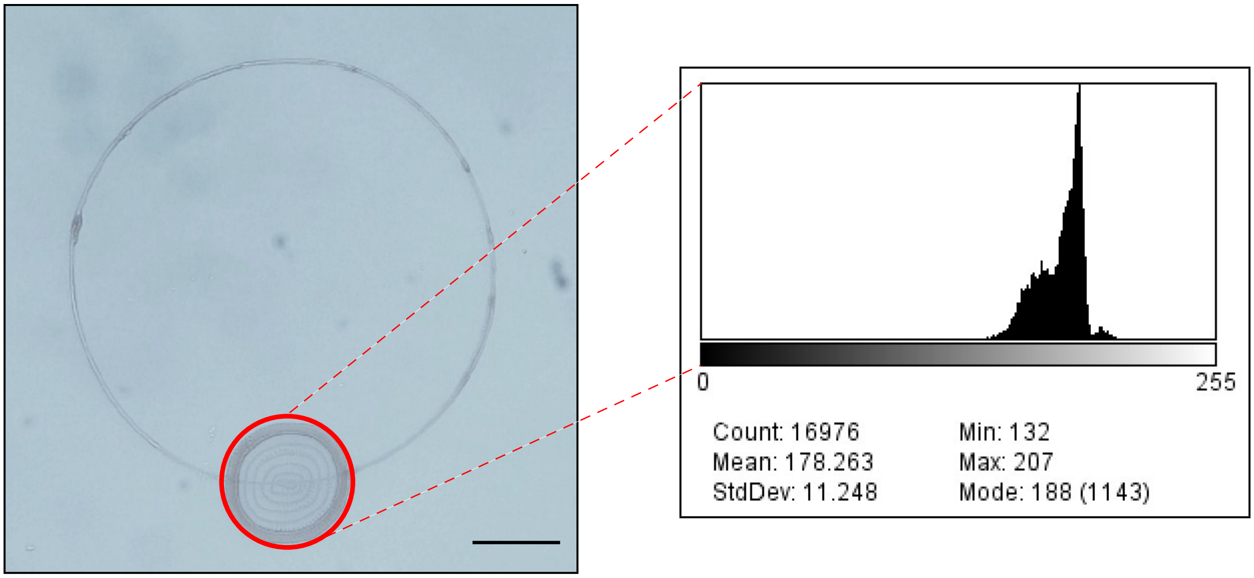


***Figure S8**: Greyscale histograms for patch areas were obtained from Image J. Scale bar is 100µm.*

***Table S1:** Colour intensity calculations. Red values represent the greyscale of the background which were manually set to 0.*

Greyscale Value (A)	Counts (B)	A*B
185	810	149850
186	957	178002
187	1101	205887
188	1143	214884
189	860	162540
190	0 (background)	0
191	0 (background)	0
192	0 (background)	0
	$\sum_{0}^{255}(B)$	$\sum_{0}^{255}(A*B)$
	14531	2557801
Average greyscale value:	$\sum_{0}^{255}(A*B) \Big/ \sum_{0}^{255}(B)$ = 176.02	

Droplet Pop Consistency

SET dimensions affect the consistency of the droplet pop. A poor droplet pop causes analyte to deposit around the ring periphery (Figure S9A). Optimization of SET dimensions leads to a good quality droplet pop where analyte is successfully concentrated within the patch (Figure S9B).

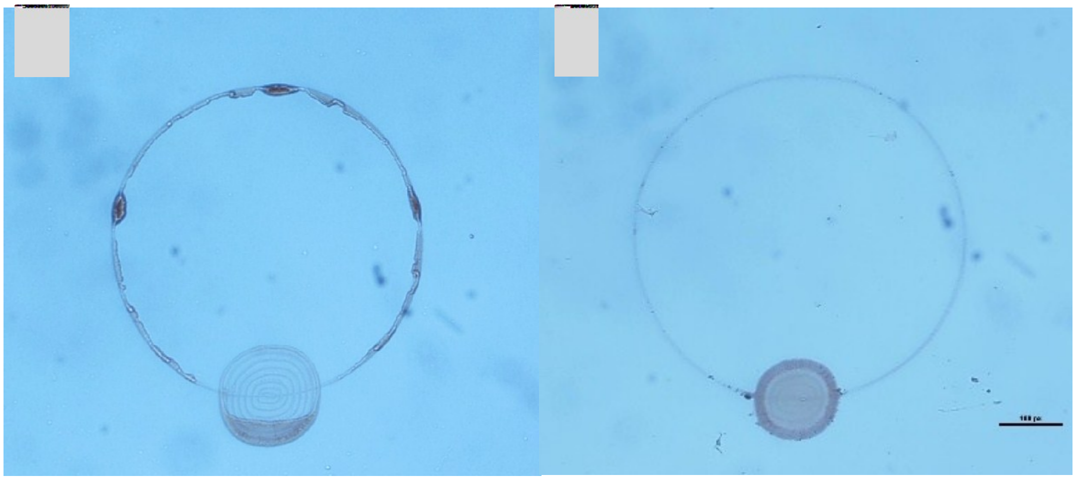


Figure S9*: Comparison of a (A) poor quality droplet pop leading to analyte distribution around the periphery, and (B) a good quality droplet pop where analyte is confined within the patch. Both SETs were fabricated at 0.5 mW and 10 laser passes. Scale bar is 100µm.*

Uniformity of Evaporation

Uniformity of evaporation in the developed device is demonstrated in Figure S10. The plot shows surface intensity profiles of Allura Red droplets evaporated on three SET types. The coffee ring effect can be seen in the milled circle (40 pixels and 900 pixels) and in the ring (10 pixels/100 pixels) and 850 pixels/975 pixels) by the sharp peaks at the edges. Similarly, the coffee ring effect is seen in the ring/patch design (800 pixels and 1000 pixels), but the signal has been confined to a much smaller area and the absolute intensity of the patch region is stronger. It should be noted that despite the grey value baselines of the three plots do not exactly match, we are ultimately evaluating the relative intensity signals in the areas of interest. Figure S11 is added for visualization of the x-coordinates.

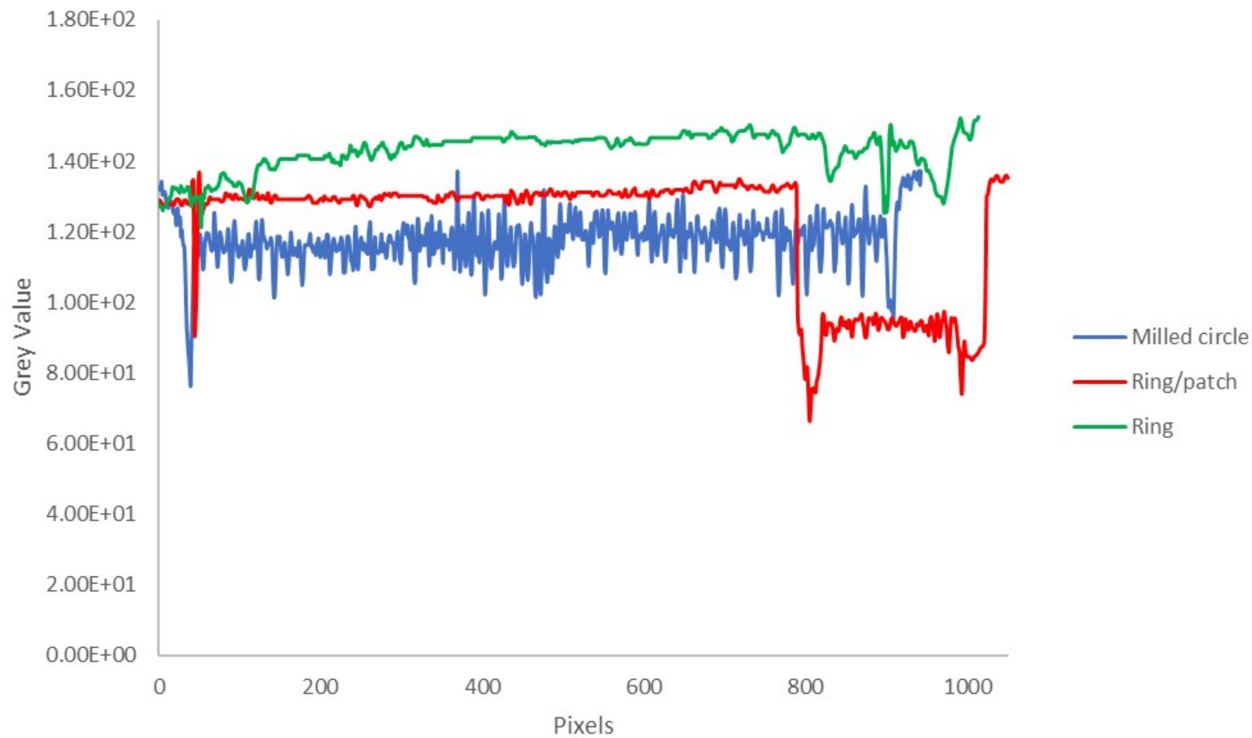


***Figure S10**: Surface intensity profiles of Allura Red droplets evaporated on three SET types.*

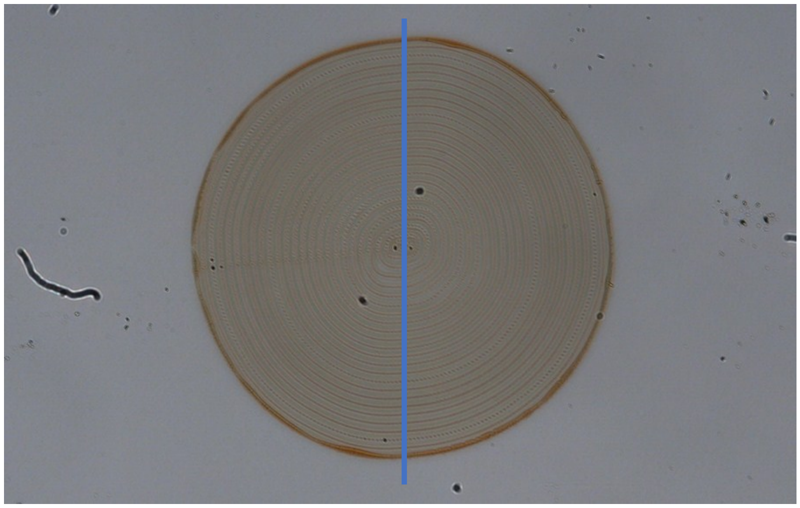


***Figure S11**: A milled circle SET (0.5mW, 10 passes) following evaporation of a droplet of Allura Red. The blue trace drawn over the SET represents the x-coordinate in Figure S10.*