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

Supplementary Information for

Microfabricated Porous Layer Open Tubular (PLOT) Column

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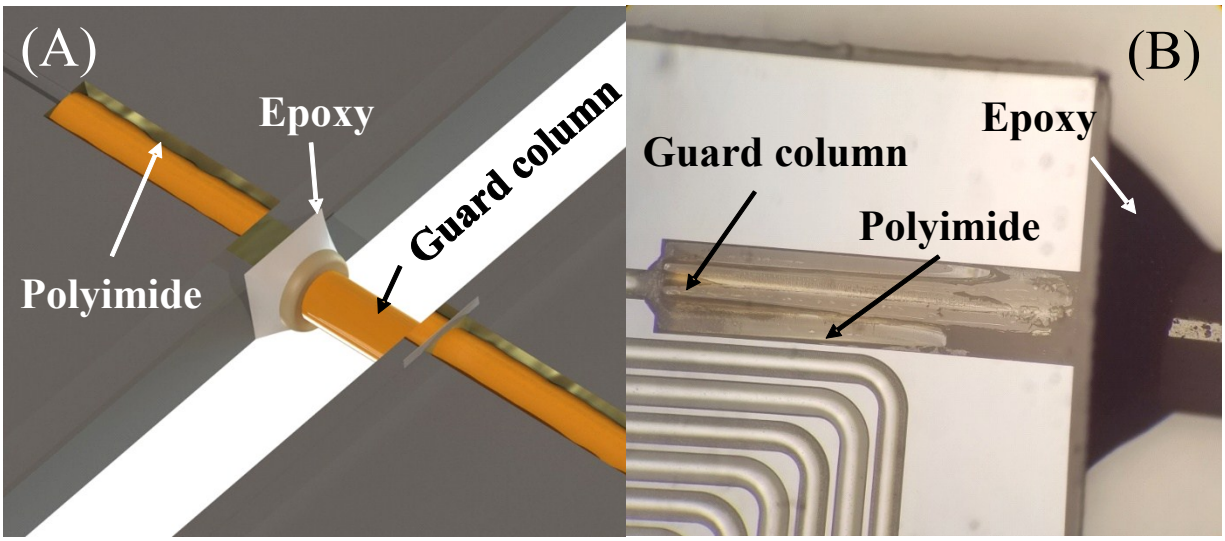

Figure S1. (A) Illustration of hybrid adhesive connection ports. (B) Photo of the connection port.

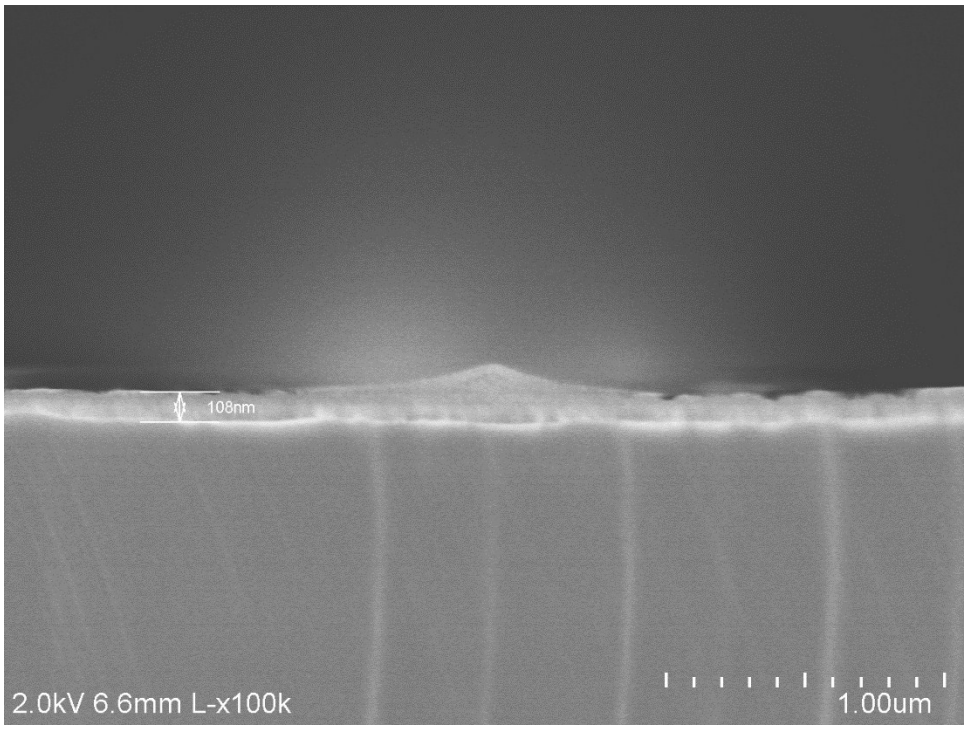

Figure S2. SEM image of film along column wall, with a thickness of approximately 108 nm. This thickness was not included in the calculation for average film thickness due to being much smaller than the amount of stationary phase pooled at the column corners.

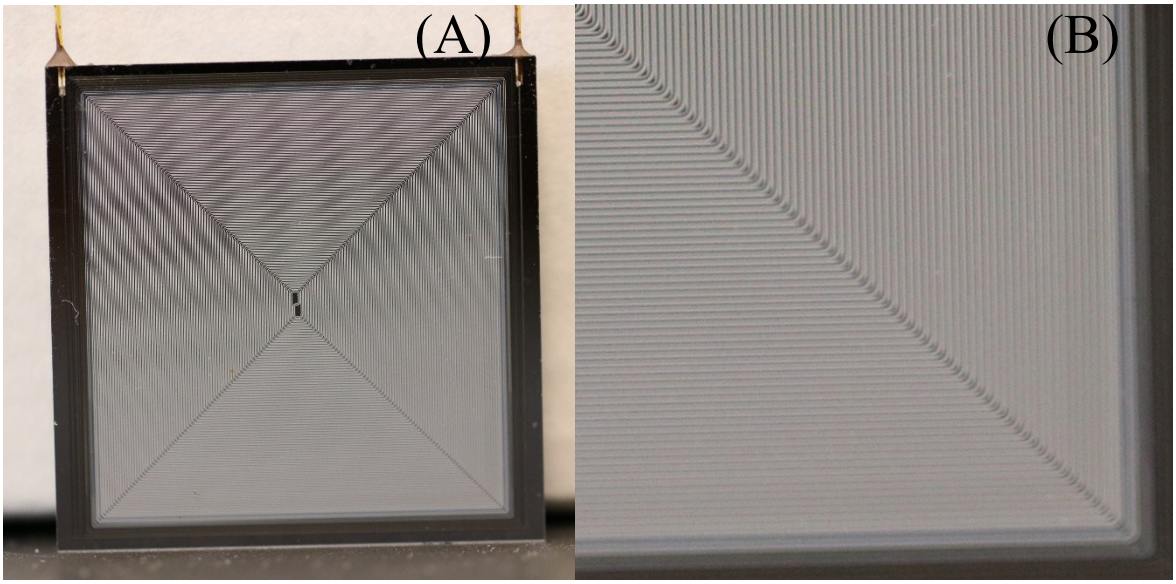

Figure S3. (A) Photograph of µPLOT column. (B) Zoom-in of µPLOT channel pattern.

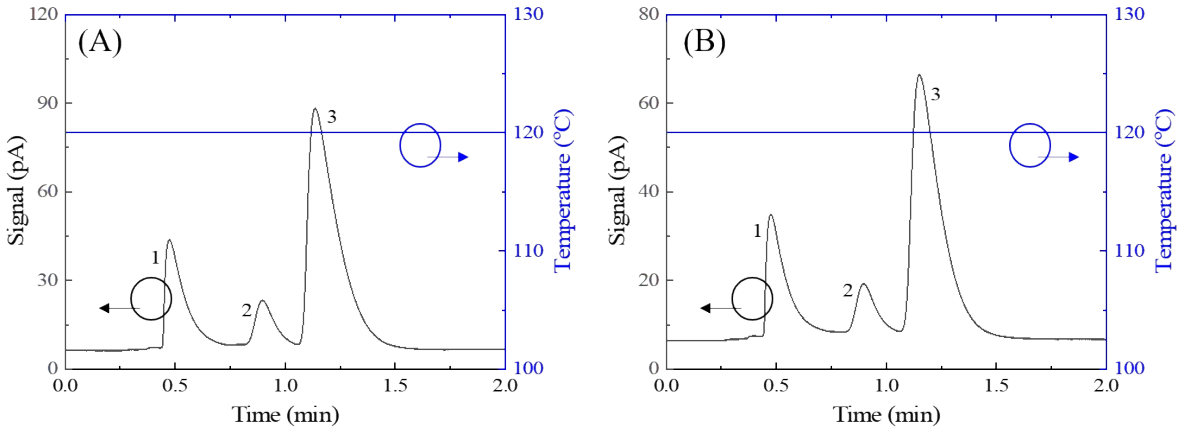

Figure S4. Separation of methanol(1), ethanol(2), and formaldehyde(3) with no added moisture (A) and with 1 µL of additional liquid water (B). A solution of formaldehyde, methanol, and ethanol was heated to 80 °C and 50 µL of headspace vapor was subsequently drawn for injection. Carrier gas flow rate: 1.3 mL/min at 120 °C. Analysis is provided in Table S1.

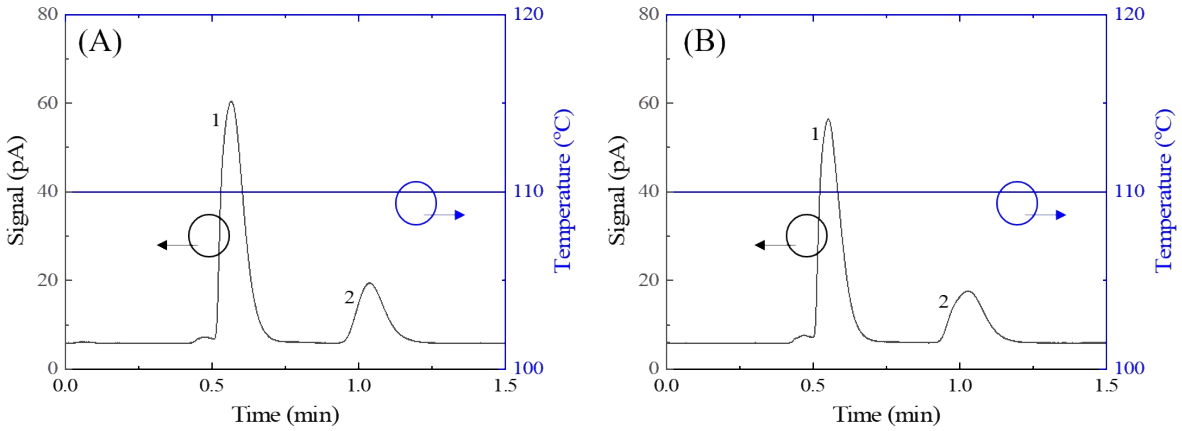

Figure S5. Separation of nonane(1) and dodecane(2) using an in-house coated OV-5 column (coating procedure detailed below). An injection of 100 µL of headspace vapor from a mixture of the two analytes was made with no added moisture (A) and with 50 µL of additional water vapor (B). The water was heated to 80 °C in order to increase the partial pressure in the headspace. Carrier gas flow rate: 1.3 mL/min. Analysis is provided in Table S2.

Coating procedure. OV-1 (75% w/w), OV-17 (10% w/w), and Dow SYLGARD™ 184 reagent B (15% w/w, crosslinker) were dissolved in dichloromethane to create a 2% (w/w) coating solution (effectively a 5% phenyl stationary phase). A 5 m long capillary column (250 µm i.d.) was silanized prior to coating by 8 repeated injections of hexamethyldisilazane (HMDS) vapor. Subsequently, an 80 µL coating solution was loaded into the capillary from the column inlet and driven out through a 1 m dummy column (250 µm i.d.), which ensured a constant coating plug speed (1 cm/min). After coating, dry air was continuously flowed through the column for 2 hours, followed by crosslinking at 80 °C for another 2 hours and subsequent deactivation using HMDS. The column was then aged at 230 °C for 3 hours under a helium flow of 0.5 mL/min.

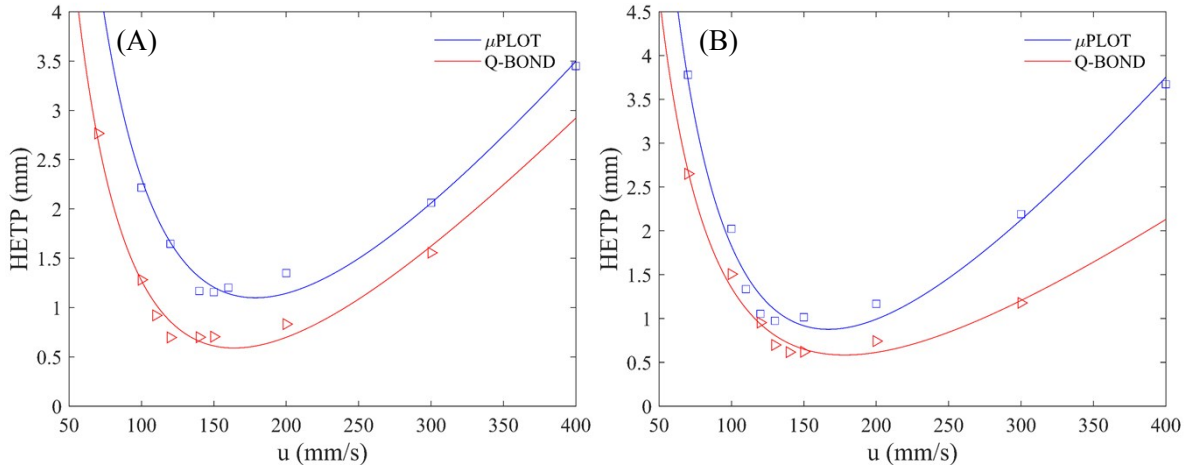

Figure S6. Golay plots with height equivalents to theoretical plates (HETPs) measured for µPLOT and a 5 m long RESTEK Q-BOND. (A) HETP for methanol at a temperature of 105 °C. (B) HETP for butane at a temperature of 130 °C. See Table S3 for more information.

	Dry	1 μL	p-value
Methanol[(1)] RT	0.477±0.0026	0.453±0.0066	0.0005
Methanol[(1)] FWHM	0.102±0.0011	0.108±0.0099	0.2202
Ethanol[(2)] RT	0.898±0.0019	0.885±0.0127	0.0798
Ethanol[(2)] FWHM	0.080±0.0002	0.083±0.0828	0.1918
Formaldehyde[(3)] RT	1.148±0.0075	1.149±0.0147	0.9119
Formaldehyde[(3)] FWHM	0.145±0.0008	0.148±0.0061	0.4272

Table S1. p-values between retention times (RTs) and FWHMs of methanol, ethanol, and formaldehyde with no added moisture and 1 μL of added moisture (5 runs each). Significance was taken at $p = 0.05$. Methanol's retention time was significantly lower with added moisture. All other p-values are over 0.5, showing no significant differences (notably, added moisture did not significantly broaden any peaks).

	Dry	50 µL	p-value
Nonane[(1)] RT	0.563±0.005	0.552±0.004	0.051
Nonane [(1)] FWHM	0.084±0.006	0.095±0.002	0.049
Dodecane[(2)] RT	1.038±0.004	1.032±0.003	0.088
Dodecane[(2)] FWHM	0.113±0.003	0.141±0.004	0.016

Table S2. p-values between retention times (RTs) and FWHMs of nonane and dodecane with no added moisture and 50 µL of added moisture (5 runs each). Significance was taken at $p = 0.05$. Both peaks were significantly broadened with added moisture, showing that the OV-5 column does not exhibit the same moisture resistance that the µPLOT does.

	HETP (mm)
μPLOT in this work (Methanol)	1.156
μPLOT in this work (Butane)	0.974
Restek Q-BOND (Methanol)	0.697
Restek Q-BOND (Butane)	0.617
Ref. [S1] (Butane)[1]	~0.2
Ref. [S2] (Methanol)[2]	~0.25
Refs. [S3] and [S4] (Butane)[3,4]	~0.35

Table S3. Height equivalents to theoretical plates (HETPs) for divinylbenzene-based PLOT (μPLOT, Q-BOND, and Refs. [S1] and [S2]) and silica-based (Refs. [S3] and [S4]) porous layer columns. HETPs for the μPLOT and Q-BOND were measured based on optimized values obtained from Golay plots (see Figure S6). Other HETPs were estimated based on plots provided in the respective references.

References

S[1] Korolev, A. A.; Shiryaeva, V. E.; Popova, T. P.; Kozin, A. V.; D'yachkov, I. A.; Kurganov, A. A. Macroporous polymeric monoliths as stationary phases in gas adsorption chromatography. *Polym. Sci. Ser. A* **2006**, *48*, 779-786.

S[2] Nesterenko, E. P.; Burke, M.; de Bosset, C.; Pessutto, P.; Malafosse, C.; Collins, D. A. Monolithic porous layer open tubular (monoPLOT) capillary columns for gas chromatography. *RSC Advances* **2015**, *5*, 7890-7896.

S[3] Korolev, A. A.; Shiryaeva, V. E.; Popova, T. P.; Kurganov, A. A. Effect of the pressure of the carrier gas on the parameters of the Van Deemter equation for monolithic silica gel gas chromatography columns. *Russ. J. Phys. Chem.* **2006**, *80*, 781-785.

S[4] Korolev, A. A.; Shiryaeva, V. E.; Popova, T. P.; Kurganov, A. A. A study of the efficiency of monolithic silica gel capillary columns for gas chromatography. *Russ. J. Phys. Chem.* **2006**, *80*, 609-614.