**Supporting Information** 

# The development of a disposable gas chromatography microcolumn

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# **Materials and Methods:**

## **General Notes:**

Polymeric materials: two-part flexible epoxies (3M DP-190, DP-125, and DP-105) and polydimethylsiloxane two-part kit (Dow Corning Sylgard 184). The polyvinylidene difluoride substrate for the colorimetric sensor arrays was purchased from Pall Corporation. All other reagents were purchased from Aldrich and used without further purification.

## **SEM Imaging:**

Scanning electron micrographs were obtained on a JEOL 7000F instrument operating at 10 kV with a medium probe current and a working distance of 10 mm. Samples were mounted to the holder via carbon tape and sputter coated with approximately 10 nm of Au/Pd prior to analysis to prevent surface charging.

## AFM Imaging:

Atomic force micrographs were obtained on an Asylum Research MFP-3D instrument operating in tapping mode. Scans were done in air using a Tap300Al-G tip. Samples were subjected to the same fabrication procedure and conditions as the polymer microcolumns but were cast and cured against a piece of polished flat of PCTFE instead of the microcolumn mold. The AFM image (Figure 1f) shows two domains with distinctly different materials properties: a softer domain (lighter regions) and a rigid domain (darker regions). One expects the siloxane-rich domains to be softer than the cured epoxy (the monomer used to form PDMS is diethoxydimethylsilane, DEDMS, which has no ability to cross-link); as such, the lighter regions have been attributed to the siloxane-rich phase. Surprisingly, even though the bulk doping percentage of the DEDMS is 10 wt%, ~50% surface coverage (analyzed using the ImageJ software package from NIH) of these softer domains is observed. This is consistent with the hypothesis that silane species phase separate and migrate preferentially to the surface.

# TOF-SIMS:

TOF-SIMS experiments were done using a PHI TRIFT III instrument with a pulsed liquid metal  $Au_1^+$  ion gun (3 nA, unbunched). A typical scan size was 50 microns with 32 sec analysis time. Positive secondary ions with a mass range of 0-2000 amu were

acquired, and charge compensation was used. Samples of the described silane/epoxy composite were cast and cured in a PCTFE microcolumn mold as usual. Once removed from the mold, portions of the channel wall were sectioned and fully cured at 70 °C prior to analysis. The TOF-SIMS spectra of the channel surface (Figure S4) shows characteristic peaks for polydimethylsiloxane.<sup>1</sup> The presence of peaks at 207, 221, and 281 demonstrate that condensation of DEDMS has indeed occurred (M/Z value of DEDMS<sup>+</sup> is 147 amu); the boiling point of DEDMS is 114 °C, and without polymerization to a higher boiling point (lower vapor pressure) oligomer, the silane species would have evaporated during curing.

# **Microcolumn Formulation:**

Polymerization reactions of the organosilane (DEMDS) and epoxy components are given in Figure S1.2-4 Organosilane additives were screened during formulation development. During this screening process, DEDMS was found to produce micrcolumns with the longest analyte retention relative to peak width (i.e., the highest N) of the additives tested. This formulation produces a phaseseparated composite, as demonstrated by the AFM image (Figure 1f). This phase separation appears to occur between an epoxy-rich phase and a siloxane rich-phase, i.e., the polymerizations are largely independent. One byproduct of the polymerization of epoxy is HCl, which is known to catalyze the condensation of alkoxysilanes.<sup>2, 5</sup> Alkoxysilanes form Si-O-Si bonds due their stability relative to Si-O-C or Si-N-C bonds.<sup>5</sup> The condensation of DEDMS forms cyclic and oligomeric dimethylsilicones, similar to the well-known condensation of dichlorodimethylsilane.<sup>6</sup> The product may or may not contain covalent linkages between the epoxy-rich and siloxane-rich regions.

A system in which cross reactions between the epoxy monomer and siloxane monomer are possible has also been examined. When 3-(glycidoxypropyl)dimethyethoxysilane (GDMES) is used as the organosilane dopant, coupling of the glycidoxypropyl group to the majority phase epoxide occurs. For the resulting polymer, phase separation is not observed and the retention time of analytes eluting from columns made from the linked polymer give very broad peaks similar to microcolumns made from a single permeable polymer. The epoxy functionality on the organosilane additive inhibits phase segregation of the siloxane and epoxy domains, and instead produces a more uniform polymer with higher gas permeability.

The full cure time of the flexible epoxies is ~7 days, which allows the small organosilane monomers, cyclics, and oligomers to diffuse to the surface. The surface preference of the siloxane species over the epoxy species is likely a function of the differences in the epoxy/silane surface energies. The siloxane film "thickness" may be tunable by shortening or lengthening the cure time of one or both components of the thermoset composite, which should change the diffusion characteristics of the siloxane through the polymerizing epoxy network and lead to either thicker or thinner siloxane-rich domains at the channel surface. One may hypothesize that the materials properties of the "structural" component of the thermoset composite, e.g., cure time and silane diffusivity, are more important than the chemical characteristics. Therefore, the epoxy component could hopefully be changed to another polymer with similar materials properties but less surface functionality to reduce wall activity and improve the separation of polar analytes (e.g., amines, alcohols, etc.). Further studies are needed to elucidate the optimum polymer formulation.

There were no significant differences in column performance among microcolumns made with 5 wt%, 10 wt%, and 20 wt% DEDMS doping in flexible epoxy. This is consistent with the hypothesis that the surface segregation of the polymerized DEDMS is independent of bulk silane concentrations. AFM phase images of all formulations showed similar surface coverage.

#### Microcolumn Fabrication:

The epoxy component, part B, of DP-190 (3.00 g) was first mixed with diethoxydimethylsilane (720  $\mu$ L) for one hour using a magnetic stir bar. This mixture (2.58 g) was added to the accelerator component, part A, of DP-190 (1.86 g) and mixed well. The doped epoxy was poured into the PCTFE mold and degassed under vacuum at 40 °C. The degassed polymer was then cured for 24 hours at 70 °C. The cured polymer was allowed to cool and peeled from the PCTFE mold by hand. The edges of the doped epoxy column were removed to yield a flat surface for bonding. Column dimensions were chosen based on the dimensions of similar "traditional" microcolumns in the literature, so comparisons of performance might be more relevant.

DP-125 was mixed with 10 wt% diethoxydimethylsilane. The doped epoxy (0.15 g) was immediately spread onto a glass slide via a doctor blade technique and left at room temperature for 2.5 hours to cure. The doped epoxy column was placed on the partially cured thin film, applying light pressure as needed to seal. The sealed microcolumn was cured overnight at 70 °C. It is important to note the glass is merely used for convenience, and the fully cured polymer microcolumn can be removed from the glass to form a free-standing device with no structural support.

Polyimide coated fused silica capillary tubing (IDEX; 8 cm long, 360  $\mu$ m O.D., 150  $\mu$ m I.D.) was inserted into the inlet and outlet (450  $\mu$ m width, 5 mm length) for connection to the GC injection and detector ports. DP-125 flexible epoxy was used to bond the tubing to the microcolumn and produce a leak-free seal. The finished microcolumn was cured at 70 °C for one month before testing. The optimum duration of curing (~20 to 30 days) was experimentally determined. The microcolumns are usable prior to the 20 to 30 day mark, but suffer in terms of performance; the theoretical plate count of a given microcolumn tested at day 5 is ~40% of its 30 day value,

and tested at day 20 is ~95% or its 30 day value. This aging is likely due to the time necessary for the DEDMS to polymerize to sufficiently long oligomeric chains that observed off-gassing is no longer significant.

#### Microcolumn Testing:

All experiments were performed using an HP 5890 Series II GC/FID. The carrier gas was helium set to a column head pressure of ~1 psi. Microtight unions (IDEX; part # P-772) were used to connect the microcolumn to fused silica capillary tubing (IDEX; 360 µm O.D., 150 µm I.D.) connected to the injection port and FID detector. The presence of a single flow path was confirmed from the symmetry of the methane peak. The linear velocities for each experiment were calculated from the retention time of the unretained methane peak. The split ratio for all experiments was 500:1, the inlet temperature was 250 °C, and the FID detector temperature was 300 °C. All injections were done manually, and injection volumes were ~0.3 µL. Linear velocities were chosen based on experimentally derived Golay plots of each microcolumn. When possible, linear velocities closest to the Golay minimum (~30-40 cm s<sup>-1</sup>) were used. However, sometimes pressure requirements limited the available linear velocities, in which case the attainable velocities nearest the Golay minimum were used. Data was collected at a rate of 20 Hz using Chemstation software (Rev. A.10.02), and peak finding and data analyses were performed using OriginPro 8.5.

For the reproducibility and shelf life experiment (Figure S6), a microcolumn was cured at 70 °C for twenty days before analysis and was stored at 70 °C between time points. An elevated storage temperature was chosen to accelerate any potential polymer degradation. All trials were performed at room temperature with  $u = 45 \text{ cm s}^{-1}$  and in triplicate. Multiple trials run within one day produce consistent retention times with low standard deviation. Little change in analyte retention is observed over the 50 day time period. Observed fluctuations are caused in part by changes in the GC/column/detector connections, which occur every time a microcolumn is removed and reconnected. Microcolumn performance is consistent among microcolumns made using the same initial mold (i.e., same channel dimensions) and polymer formulation.

The polymer formulation used in these microcolumns is capable of temperature programming up to 50 °C. The flexible epoxy's  $T_g$  is 45 °C. At temperatures higher than 50°C, the  $t_r$  of analytes separated using this microcolumn continue to decrease, but the FWHM begins to increase, reducing separation ability. At higher temperatures, the epoxy phase is no longer fully impermeable to analytes and begins contributing to the overall separation mechanism, which leads to wider and less symmetric peaks. A "structural" polymer with a higher  $T_g$  (as a replacement to the flexible epoxy used here) would likely improve the temperature programming capabilities.

#### **Colorimetric Sensor Array Preparation and Testing:**

The colorimetric sensor arrays were prepared as described previously.<sup>7</sup> The colorimetric sensor array consisted of a series of eight spots following the pattern sensor 1,2,3,4,1,2,3,4, where sensor 1 is  $\alpha$ -naphthyl red + p-toluenesulfonic acid, sensor 2 is tetraiodophenolsulfonephthalein, sensor 3 is fluorescein, and sensor

4 is bromocresol green. These amine sensitive spots were chosen for this initial proof-of-concept because they have been fully optimized in previous work. For a more universal gas chromatography detector, the colorimetric sensors included in the sensor array would be tailored for analytes of interest.

We have previously demonstrated these colorimetric sensors are unaffected by water vapor and do not need to be calibrated before use.<sup>7</sup> Printing quality is sufficient that inconsistencies in array response among arrays can be accounted for by subtracting the "before-exposure" image of the array from the "during-exposure" image. The sensor spot is saturated after sufficient analyte exposure; therefore the injection volume used in these experiments was set to be sufficiently small so as to allow for visualization of all eluting analytes from the microcolumn.

The colorimetric sensor array response was monitored using a Canon EOS Mark II full frame CMOS digital SLR camera in HD video mode and a 100 mm macro lens with lighting from natural white LEDs (SuperBrightLEDs.com). The array holder, Figure S7, was micromachined out of white PET. The gas flow channel was 1 cm long, 200 µm deep, and 400 µm wide. Two 370 µm diameter through-holes were drilled through the back of the holder into each end of the flow path to accommodate polyimide coated fused silica capillary tubing (IDEX; 360 µm O.D., 150 µm I.D.). These acted as the inlet and outlet for the holder. A leak free connection was made using Nanoport fittings (IDEX, N124S). Immediately surrounding the channel was a recess to accommodate a PDMS O-ring made in lab from Dow Corning's Sylgard 184. PDMS is translucent, did not interfere with imaging, and was sufficiently elastomeric to provide a leak-free seal when pressure was applied. To seal the channel, pressure was applied to a glass microscope slide (outline shown in red in Figure S7) via two clips and the lip of the holder.

#### **Image Processing and Data Analysis:**

GOM Media Player software was used to extract still frames every 33 ms from the HD video. In these images, the spots in the array are approximately 20 pixels in diameter. Spotfinder software (iSense) was used to average the RGB values for a circular area with an eight-pixel diameter in the spot center. A pixel-by-pixel digital subtraction of a before-elution image from video images during elution generates a 24-dimensional color-change vector (i.e., 8  $\Delta$ RGB values) dependent on exposure time, analyte identity, and analyte concentration. The Euclidian distance (ED) of the color change is defined as:

$$\mathsf{ED} = (\Delta \mathsf{R}_1^2 + \Delta \mathsf{G}_1^2 + \Delta \mathsf{B}_1^2 + \Delta \mathsf{R}_2^2 + \dots + \Delta \mathsf{B}_8^2)^{1/2} \qquad \mathsf{Eq. 1}$$

The values obtained from the Spotfinder software were then smoothed using 11-point adjacent averaging. The slope was calculated for the smoothed values using the following equations:

$$R_{n}' = (R_{n}-R_{n-4})/(t_{n}-t_{n-4})$$
 Eq. 2

$$G_{n}' = (G_{n}-G_{n-4})/(t_{n}-t_{n-4})$$
 Eq. 3

$$B_{n}' = (B_{n}-B_{n-4})/(t_{n}-t_{n-4})$$
 Eq. 4

where  $t_n-t_{n-4}$  is equal to 1.33 seconds. Using these slope values, an ED of the slope response was calculated and plotted with respect to time in Fig. 4.

Limits of detection (LODs) were obtained based on a single point calibration of the array response data following data analysis (see above). LODs are expressed in terms of an analyte's injection mass (i.e., mass injected on column) and are estimated using the following equation:

$$LOD = 3\sigma m_A / (S_A - S_B)$$
 Eq. 5

where  $\sigma$  is the standard deviation of the baseline noise,  $m_A$  is the mass injected onto the column (i.e., injection mass adjusted for split flow),  $S_A$  is the signal at the peak maximum for a given analyte using the slope vs. time trace, and  $S_B$  is the averaged baseline signal.  $S_A$ ,  $S_B$ , and  $\sigma$  are determined from the channel with the highest signal to noise ratio (G<sub>1</sub>, G<sub>1</sub>, and R<sub>4</sub> for propylamine, triethylamine, and piperidine, respectively).

Analyte concentrations in the peak can be estimated by using the following equation:

$$[analyte]_{at sensor} = (22.4*m_A)/(MW_A*F*t)$$
 Eq. 6

where [analyte]<sub>at sensor</sub> is the average concentration of a given analyte over the entire peak in ppmv, m<sub>A</sub> is the mass injected in nanograms onto the column (i.e., injection mass adjusted for split flow), MW<sub>A</sub> is the molecular weight of the analyte, F is the volumetric flow rate of the mobile phase at the sensor array in mL/s, and t is the peak width in seconds.

#### **Colorimetric Sensor Array Discussion:**

We have previously reported a disposable, highly sensitive colorimetric sensing array for the detection and notably, the identification of VOCs and toxic gases.<sup>7-11</sup> This technology differs from other electronic nose technologies that generally rely on weaker and less specific interactions (i.e., van der Waals and physical adsorption) by utilizing strong sensor-analyte interactions including Lewis donor-acceptor, Brønsted acid/base, and vapochromic chemoresponsive dyes. Explored here is the integration of a colorimetric sensor array with the disposable microcolumn for the separation, detection, and identification of amines as an example. Power consumption and size of readers for optical imaging can be minimal, and several battery powered handheld prototypes for field analysis using colorimentric sensor arrays have been developed by our lab.

To probe the feasibility of a colorimetric sensor for GC, a mixture of three amines was injected onto the previously described microcolumn at room temperature, and the response of the eluent was recorded with either an FID or a colorimetric sensor array. Amines are prone to hydrogen bonding to surfaces, especially those with surface functionality, as is present in the epoxy formulation, which causes broadening in GC elutions, as shown in Figure 4. Use of a different impermeable polymer as an alternative to the flexible epoxy could diminish such tailing.

Figure S8a shows the time derivative ED versus time response profile of the array; as expected, a jump in array response is observed

as each analyte elutes from the column. The array response is dependent on analyte concentration, and therefore one expects the largest change in ED to occur when the highest concentration of analyte passes over the detector, i.e., at each analyte's retention time. The resulting chromatogram from the colorimetric sensor array response, calculated by taking the time derivative ED of the values obtained from Eqs. 2-4, is strikingly similar to that obtained using an FID detector (Figure 4).

The FID and colorimetric sensor array chromatograms (Fig. 4) are quantitatively similar with minor differences due to the larger volume of the sensor array detector used in these studies. Band broadening is observed due to the relatively large volume of the sensor array flow cell, the data processing methods used, and the sequential arrangement of the colorimetric spots. It is expected that the broadening should be significantly reduced with optimization of the configuration of the array and array holder. Spot response, in this case, is dependent on both spot identity and spot position; the current arrangement of spots also contributes significantly to band broadening. These effects may be remedied by switching to colorimetric "bars" that are side-by-side and aligned parallel to gas flow.

As can be seen in Figure S8b-i, all spots respond to the amine mixture, and the spots with the highest responses are different for each analyte suggesting the array may be useful in providing chemical classification or identifying chemical unknowns. The time derivative of ED is shown in Figure 4 as a simple visualization of the overall array response and would not be used in either the chemical identification of unknowns or the calculations of LODs. For these single channel data,  $\Delta R$ ,  $\Delta G$ , and  $\Delta B$  values, would be used.

The LODs of these three amines from injections of known amounts with known flow rates through the microcolumns were calculated using Eq. 5. For propylamine, triethylamine and piperidine, the calculated method LODs (i.e., mass injected on column) are 10, 10, and 35 ng, respectively. The method LODs calculated using the FID detector data are 3, 1, and 8 ng, respectively, which is only a minor improvement over the non-optimized colorimetric array. The largest contributor to noise in the imaging technique is movement of the imaging device (i.e., camera) with respect to the array.<sup>12</sup> A substantial improvement in noise, and therefore significantly lower LODs, is expected with an imaging device configuration where the imager (e.g., photodiode or color contact image sensor) is completely immobile with respect to the array. For colorimetric sensor arrays used for the detection and identification of toxic industrial chemicals, LODs for amines are extrapolated to be ~40 pg/mL after 5 minutes of exposure.<sup>7, 10</sup> LODs obtained in this work are consistent with those results, given the few second exposure times inherent for a GC detector. Using Eq. 4, the peak concentrations were determined to be ~100 ppmv. These results demonstrate a respectable proof of concept for a fully disposable gas chromatography microcolumn-colorimetric array detector.

#### References

- Z. Y. Michael T. Timkoa, Jesse Krolla, John T. Jaynea, Douglas R. Worsnopa, Richard C. Miake-Lyea, Timothy B. Onascha, David Liscinskyb, Thomas W. Kirchstetterc, Hugo Destaillatsc, Amara L. Holderd, Jared D. Smithe & Kevin R. Wilsone, *Aerosol Sci. Tech.*, 2009, 43, 855-865.
- 2. F. de Buyl, Int. J. Adhes. Adhes., 2001, 21, 411-422.
- B. Arkles, Larson, G. L., Ed., Silicon Compounds: Silanes & Silicones, 5000A, 3rd ed, Gelest Inc, Morrisville, PA., 2013.
- J.-P. Pascault and R. J. J. Williams, in *Epoxy Polymers: New materials and innovations*, eds. J.-P. Pascault and R. J. J. Williams, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, 2010, pp. 1-12.
- C. J. Brinker and G. W. Scherer, *The Physics and Chemistry of Sol-Gel Processing*, Academic Press, Inc., San Diego, CA, 1990.
- L. C. Klein, Sol-Gel Optics: Processing and Applications, Kluwer Academic Publishers, 1994.
- H. L. Sung, F. Liang, J. W. Kemling, C. J. Musto and K. S. Suslick, Nat. Chem., 2009, 1, 562-567.
- 8. N. A. Rakow and K. S. Suslick, Nature, 2000, 406, 710-713.
- M. C. Janzen, J. B. Ponder, D. P. Bailey, C. K. Ingison and K. S. Suslick, *Anal. Chem.*, 2006, 78, 3591-3600.
- L. Feng, C. J. Musto, J. W. Kemling, S. H. Lim, W. Zhong and K. S. Suslick, *Anal. Chem.*, 2010, 82, 9433-9440.
- J. R. Askim, M. Mahmoudi and K. S. Suslick, *Chem. Soc. Rev.*, 2013, 42, 8649-8682.
- M. K. LaGasse, J. M. Rankin, J. R. Askim and K. S. Suslick, Sensor. Actuat. B-Chem., 2014, 197, 116-122.

Table 51. Retention times (tr) and full width at half maximum (w(1/2)) values for n-alkanes separated using DEDMS doped epoxy microcolumns. Chromatograms shown in Figure 3a,c.

	methane	<i>n</i> -pentane		<i>n-</i> hexane		<i>n-</i> heptane		<i>n-</i> octane		<i>n-</i> nonane		<i>n-</i> decane	
(s)	t <sub>r</sub>	t <sub>r</sub>	W <sub>(1/2)</sub>	t <sub>r</sub>	W <sub>(1/2)</sub>	tr	W <sub>(1/2)</sub>	tr	W <sub>(1/2)</sub>	tr	W <sub>(1/2)</sub>	t <sub>r</sub>	<b>W</b> <sub>(1/2)</sub>
250 μm x 500 μm x 1 m (Figure 3a) <sup>a,b</sup>	3.7	4.1	0.32	5.7	0.61	10.4	1.2	23.3	2.7	58.8	6.4	157	17.9
100 μm x 500 μm x 1 m (Figure 3b) <sup>a,c</sup>	2.4	3.2	0.19	5.0	0.28	10.1	0.54	24.0	1.3	62.5	3.4	173	9.7

<sup>a</sup> Manual injections of ~ 0.3 µL of *n*-alkane mixture; 500:1 split ratio; injection temperature 250 °C

Flame ionization detector (FID) used; FID temperature 300 °C

Column held at room temperature (~23 °C) <sup>b</sup> Linear velocity (u) = 30 cm s<sup>-1</sup>; F = 2.3 mL min<sup>-1</sup> <sup>c</sup> Linear velocity (u) = 55 cm s<sup>-1</sup>; volumetric flow rate at outlet (F) = 1.7 mLmin<sup>-1</sup>



b



Figure S1. Polymerization reactions for the (a) epoxy (DP-190) and (b) organosilane (DEDMS) components of the thermoset polymer composite.4,6



*Figure S2.* SEM micrographs of the moulded polymer microcolumn. (a) Channel cross-section. (b) Channel turns. (c) Channel inlet or outlet. (d) Cross-section of microcolumn sealed with thin film. Scale bars represent 250 μm.



**Figure S3.** Separation of *n*-alkanes with microcolumns made from various polymer materials. All microcolumns are 1 m long and have a crosssection geometry of 250 x 500  $\mu$ m. (1) methane, (2) butane, (3) *n*-pentane, (4) *n*-hexane, (5) *n*-heptane, (6) *n*-octane, (7) *n*-nonane, (8) *n*-decane. (a) PDMS polymer microcolumn. Linear velocity limited by fragile nature of column material, u = 16 cm s<sup>-1</sup>, F = 1.2 mL min<sup>-1</sup>, temperature programmed: 30 °C for 1 minute, ramp at 20 °C/min, hold at 100 °C. (b) DP-190 polymer microcolumn, u = 65 cm s<sup>-1</sup>, F = 4.9 mL min<sup>-1</sup>, isothermal at room temperature. (c) DP-105 polymer microcolumn, u = 50 cm s<sup>-1</sup>, F = 3.8 mL min<sup>-1</sup>, isothermal at 35 °C. Inset is an optical micrograph of the DP-105 column showing bubbles in contact with the gas flow path.



Figure S4. TOF-SIMS of a doped epoxy microcolumn wall, characteristic peaks for poly(dimethylsiloxane) are labelled with m/z values.<sup>1</sup>



*Figure S5.* Optical micrographs of doped epoxy microcolumn. (a) Image of channel turns, defect-free pathway is evident. (b) Enlarged view of channel showing the transfer of micromachining details.



*Figure S6.* Retention times of various *n*-alkanes eluted from a 1 m long doped epoxy microcolumn with a cross-section geometry of 250 x 500  $\mu$ m. All trials were performed at room temperature, with u = 45 cm s<sup>-1</sup>, F = 3.4 mL min<sup>-1</sup>, and in triplicate (standard deviation shown).



Figure S7. Image of colorimetric sensor array holder. The red dashed line shows the outline of the glass slide used to seal the channel.



*Figure S8.* Colorimetric sensor array response for a series of three amines eluting from the previously described polymeric microcolumn (cf. Fig. 4). Analytes: (1) propylamine, (2) triethylamine, and (3) piperidine; isothermal at RT;  $u = 30 \text{ cm s}^{-1}$ ;  $F = 2.3 \text{ mL min}^{-1}$ . (a) Time derivative of the Euclidean distance (ED) response profile from all spots. (b-i) Time derivative of ED for each individual sensor spot. (b) spot 1; (c) spot 2; (d) spot 3; (e) spot 4; (f) spot 5; (g) spot 6; (h) spot 7; (i) spot 8.